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(54) Title: THERMOPLASTIC ELASTOMERIC COPOLYMERS AND HAIR AND SKIN CARE COMPOSITIONS CONTAINING THE SAME (57) Abstract The present invention relates to water or alcohol soluble or dispersible thermoplastic elastomeric copolymers and to cosmetic and pharmaceutical compositions containing these copolymers. This invention especially relates to copolymers useful for hair styling purposes, and to hair styling compositions containing these copolymers. This invention further relates to copolymers useful for providing cosmetic and pharmaceutical compositions for topical application to the skin. These topical skin care compositions are useful for delivering and/or transdermally transporting active ingredients to or through the skin.		

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THERMOPLASTIC ELASTOMERIC COPOLYMERS AND HAIR AND SKIN CARE
COMPOSITIONS CONTAINING THE SAME

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TECHNICAL FIELD

10 The present invention relates to water or alcohol soluble or dispersible thermoplastic elastomeric copolymers and to cosmetic and pharmaceutical compositions containing these copolymers. These copolymers are useful for hair setting and styling purposes. A particularly useful application for these copolymers is in hair spray and mousse compositions. This invention further relates to copolymers useful for incorporating into cosmetic and pharmaceutical compositions for topical application to the skin. 15 Skin care compositions containing these copolymers are useful for delivering and/or transdermally transporting a wide variety of active ingredients to and/or through the skin.

BACKGROUND OF THE INVENTION

20 In the hair care area, the desire to have hair retain a particular style or shape is widely held. Such style retention is generally accomplished by either of two routes: permanent chemical alteration of the hair fiber or temporary alteration of hair style or shape. A temporary alteration is one which can be removed by water or by shampooing. Temporary style alteration has generally 25 been accomplished by application of a composition to dampened hair after shampooing and/or conditioning and prior to drying and/or styling. Products in the form of mousses, gels, lotions, or sprays are most commonly used for this purpose. Once the desired style is achieved, spray products are commonly used to help retain the style. These various hair care products utilize a variety of 30 gums and resins for providing styling and retention. However, the gums and resins currently used tend to feel either too sticky or too stiff upon the hair. Also, these gums and resins do not wash out as easily as desired. Therefore, the need exists for improved styling and style retention materials which provide a strong, 35

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lasting, hold without being either too stiff or too sticky, and yet which are easily removed by shampooing. Furthermore, because most hair care styling compositions are water and/or alcohol based, it is necessary that these materials have good solubility or dispersibility in these bases.

Thermoplastic elastomeric copolymers are well known. These copolymers combine thermoplastic properties, which give them solubility and strength, with rubber-like elastic properties, which give them flexibility and shape retention. However, despite these highly desirable properties, most thermoplastic elastomeric copolymers are generally insoluble or poorly soluble in water and/or alcohol systems and would not be suitable in hair care compositions. Therefore, thermoplastic elastomeric copolymers having good water and/or alcohol solubility would be useful for developing improved hair care compositions.

In the present invention new classes of thermoplastic elastomeric copolymers have been developed which have the desired flexibility, strength, and elastic properties and yet are readily soluble and/or dispersible in water and/or alcohol systems. Furthermore, these materials provide hair care compositions which leave the hair feeling natural, i.e. not stiff.

In addition to the hair care benefits provided by these copolymers, it has been found that these materials are also useful for incorporation into a wide variety of cosmetic and pharmaceutical compositions for topical application to the skin. These copolymers provide topical compositions which are more easily and uniformly spread upon the skin, which feel good upon the skin, and yet which are highly substantive. Furthermore, these copolymers are useful for enhancing the penetration of a wide variety of cosmetic and pharmaceutical actives into the skin, or alternatively, through the skin for systemic delivery.

It is an object of the present invention to provide novel, water and/or alcohol soluble and/or dispersible thermoplastic elastomeric copolymers.

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It is another object of the present invention to provide novel thermoplastic elastomeric copolymers useful in hair care compositions.

5 It is another object of the present invention to provide novel hair care compositions having improved styling and/or hold properties and having improved aesthetics.

It is another object of the present invention to provide novel thermoplastic elastomeric copolymers useful in topical skin care cosmetic and pharmaceutical compositions.

10 It is another object of the present invention to provide novel topical cosmetic and pharmaceutical compositions useful for delivering a wide variety of cosmetic materials and pharmaceutical actives to and/or through the skin.

15 These and other objects will become readily apparent from the detailed description which follows.

SUMMARY OF THE INVENTION

The present invention relates to a water or alcohol soluble or dispersible thermoplastic elastomeric copolymer having a backbone and two or more polymeric pendant side chains, said
20 copolymer formed from the copolymerization of randomly repeating A and B units wherein said copolymer comprises:

- (i) from about 40% to about 90% by weight of said A units, wherein said A units are polymerizable monomer units; and
- 25 (ii) from about 10% to about 60% by weight of said B units, wherein said B units are hydrophilic macromonomer units copolymerizable with A, whereby said macromonomer units form said pendant polymeric side chains;

wherein said copolymer has a weight average molecular weight greater than about 10,000, and wherein said copolymer exhibits two
30 distinct T_g values, said first T_g corresponding to said backbone and having a value less than about 0°C , and said second T_g corresponding to said side chains and having a value greater than about 25°C .

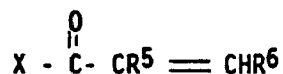
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The present invention also relates to a water or alcohol soluble or dispersible thermoplastic elastomeric copolymer having a backbone and two or more polymeric side chains, said copolymer formed from the copolymerization of randomly repeating A and B units and corresponding to the formula

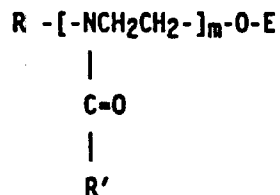


wherein A is at least one polymerizable monomer unit corresponding to the formula



wherein X is selected from the group consisting of -OH, -OM, -OR⁴, -NH₂, -NHR⁴, and -N(R⁴)₂; M is a cation selected from the group consisting of Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺, Zn⁺⁺, NH₄⁺, alkylammonium, dialkylammonium, trialkylammonium, and tetraalkylammonium; each R⁴ is independently selected from the group consisting of H, C₁-C₈ straight or branched chain alkyl, N,N-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl; and R⁵ and R⁶ are independently selected from the group consisting of H, C₁-C₈ straight or branched chain alkyl, methoxy, ethoxy, 2-hydroxyethoxy, 2-methoxyethyl, and 2-ethoxyethyl.

B is at least one hydrophilic macromonomer unit copolymerizable with A corresponding to the formula

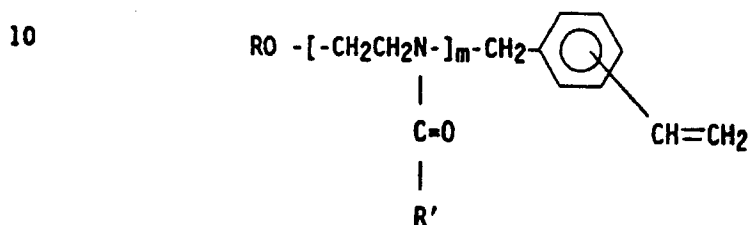


wherein E is an ethylenically unsaturated moiety, copolymerizable with A, selected from the group consisting of vinyl, allyl,

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acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzoyl, and 4-vinylbenzoyl; R and R' are independently selected from the group consisting of H and C₁-C₈ straight or branched chain alkyl; m is an integer from about 10 to about 2000; a is an integer of about 100 or greater; and b is an integer of about 2 or greater.

In further embodiments, B is at least one hydrophilic macromonomer unit copolymerizable with A corresponding to the formula



wherein R and R' are independently selected from the group consisting of H and C₁-C₈ straight or branched chain alkyl; m is an integer from about 10 to about 2000; a is an integer of about 100 or greater; and b is an integer of about 2 or greater.

In further embodiments, B is at least one hydrophilic macromonomer unit copolymerizable with A corresponding to the formula



wherein E is an ethylenically unsaturated moiety, copolymerizable with A, selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzoyl, and 4-vinylbenzoyl, and mixtures thereof; R'' is selected from the group consisting of C₁-C₄₀ straight or branched chain alkyl; R³ is selected from the group consisting of H, and C₁-C₈ straight or branched chain alkyl; m is an integer from about 20 to about 2000;

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a is an integer of about 100 or greater; and b is an integer of about 2 or greater.

5 In further embodiments, the present invention relates to hair care compositions, especially hair setting and styling compositions, containing these copolymers.

10 In further embodiments, the present invention relates to cosmetic and pharmaceutical compositions containing these copolymers for topical application to the skin for the delivery of cosmetic materials and pharmaceutical actives onto, into and/or through the skin.

15 All percentages and ratios used herein are by weight of the total composition and all measurements made are at 25°C, unless otherwise designated. The invention hereof can comprise, consist of, or consist essentially of, the essential as well as optional ingredients and components described herein.

DETAILED DESCRIPTION OF THE INVENTION

20 The term "thermoplastic elastomeric copolymer" as used herein means that the copolymer has both thermoplastic and elastomeric properties. The term "thermoplastic elastomeric copolymer" is one familiar to those of ordinary skill in polymer science. By "thermoplastic" is meant that upon heating, the copolymer softens and upon cooling it rehardens; upon being subject to stress it begins to flow and upon removal of stress it stops flowing. By "elastomeric" is meant that the copolymer has an elastic modulus
25 such that the copolymer exhibits a resistance to deformation and has limited extensibility and retraction. In other words, the copolymer tends to recover its size and shape after deformation.

30 The term "macromonomer" is one familiar to those of ordinary skill in polymer science, and is used to describe a polymeric material containing a polymerizable moiety. A macromonomer is a macromolecular monomer. A macromonomer is essentially a very large type of monomer building block unit which can be used in a polymerization reaction to form polymers with itself, with other monomers, or with other macromonomers.
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The term "water or alcohol soluble or dispersible" as used herein means that these copolymers are either freely soluble in or dispersible (as a stable suspension) in at least one of the following solvents, or alternatively, in any combination of one of the following solvents: water, methanol, ethanol, and isopropanol. By "soluble" is meant that the copolymer is soluble in the solvent or solvents at 25°C at a concentration of at least about 20 mg/mL, more preferably about 50 mg/mL, and most preferably about 100 mg/mL. By "dispersible" is meant that the copolymer forms a stable, uniform suspension (without the addition of further materials such as emulsifiers) when combined with the solvent or solvents at 25°C at a concentration of at least about 20 mg/mL, more preferably about 50 mg/mL, and most preferably about 100 mg/mL.

Thermoplastic Elastomeric Copolymers

The copolymers of the present invention are characterized in having an elastomeric or flexible backbone and rigid, thermoplastic, hydrophilic side chains. This combination of both elastomeric and thermoplastic moieties in a single copolymer provides the unique and useful properties of these materials. The copolymers of the present invention, can also be referred to as "graft copolymers" because they can be prepared from the copolymerization of monomer units and macromonomer units. In other words, the macromonomer is "grafted" or incorporated into the copolymer.

These copolymers exhibit two distinct immiscible phases. Without being limited by theory, it is believed that the hydrophilic side chains of these copolymers are closely associated with each other, thereby existing in one phase, while the backbone of the copolymer remains in a separate phase. A consequence of this phase immiscibility is that these copolymers exhibit two distinct glass transition temperatures or, "T_g's", for the backbone and the side chains. T_g is a well known term of art in polymer science used to describe the temperature at which a polymer or portion thereof undergoes a transition from a solid or

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5 brittle material to a liquid or rubber-like material. Glass transition temperatures can be measured using standard techniques that are well known to the polymer scientist of ordinary skill in the art. One particularly useful technique for determining glass transitions is differential scanning calorimetry (also known as DSC). The glass transition phenomenon in polymers is described in Introduction to Polymer Science and Technology: An SPE Textbook, (eds. H.S. Kaufman and J.J. Falcetta), (John Wiley & Sons: 1977), which is incorporated by reference herein in its entirety.

10 The T_g of the backbone of the copolymers herein (i.e. that part of the copolymer not containing the side chains) should be less than about 0°C . Preferably the T_g of the backbone should be from about -10°C to about -130°C , more preferably from about -20°C to about -125°C , and most preferably from about -55°C to about -120°C . The T_g of the side chain of the copolymers (i.e. that part of the copolymer not containing the backbone) is greater than about 20°C . Preferably the T_g of the sidechain should be from about 25°C to about 200°C , more preferably from about 30°C to about 175°C , and most preferably from about 35°C to about 150°C .

20 Because these copolymers possess two distinct T_g 's, these copolymers are useful in hair styling and setting compositions. Without being limited by theory, it is believed that when these copolymers are subjected to temperatures above both T_g 's, they are essentially liquid and can provide great flexibility during the styling process (e.g., when curling irons, blow driers, and other heat sources are applied to the hair). Upon cooling of the copolymer to room temperature (e.g., when the heat source is removed from the hair) the copolymer is then at a temperature that is typically between both T_g 's, and the copolymer possesses structural rigidity from the macromonomer side chains, and yet has flexibility from the backbones, and can provide a strong, yet flexible, hair hold or style retention.

30 Furthermore, at skin temperatures, these copolymers would be at a temperature which is essentially between both T_g 's. These copolymers can enhance the film forming properties of skin care

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compositions, and provide benefits such as better and more even distribution upon the skin.

5 The copolymers of the present invention are formed from the copolymerization of randomly repeating A and B units, preferably wherein the A units are selected from at least one polymerizable, ethylenically unsaturated monomer unit, and the B units are selected from at least one hydrophilic macromonomer unit which contains an ethylenically unsaturated moiety which is copolymerizable with A. In typical embodiments of these
10 copolymers, the backbone is primarily derived from the ethylenically unsaturated portion of the A monomer unit and the ethylenically unsaturated portion of the B macromonomer unit. The side chains are derived from the non-copolymerized portions of the macromonomer. The A and B units can be selected from a wide
15 variety of structures as long as the limitations of the copolymer are met (e.g., solubility, T_g's, and molecular weights).

The A monomer units of the copolymers of the present invention can comprise from about 40% to about 90%, more preferably from about 50% to about 85%, and most preferably from
20 about 60% to about 80%, by weight, of the copolymers.

The hydrophilic B macromonomer units can comprise from about 10% to about 60%, more preferably from about 15% to about 50%, and most preferably from about 20% to about 40%, by weight of the copolymers.

25 The copolymers of the present invention have a weight average molecular weight of at least about 10,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as viscosity, processing, aesthetic characteristics, formulation compatibility, etc. In general, the weight average molecular weight is less than
30 about 5,000,000, more generally less than about 2,500,000, and typically less than about 1,500,000. Preferably, the weight average molecular weight is from about 10,000 to about 5,000,000, more preferably from about 75,000 to about 1,000,000, even more
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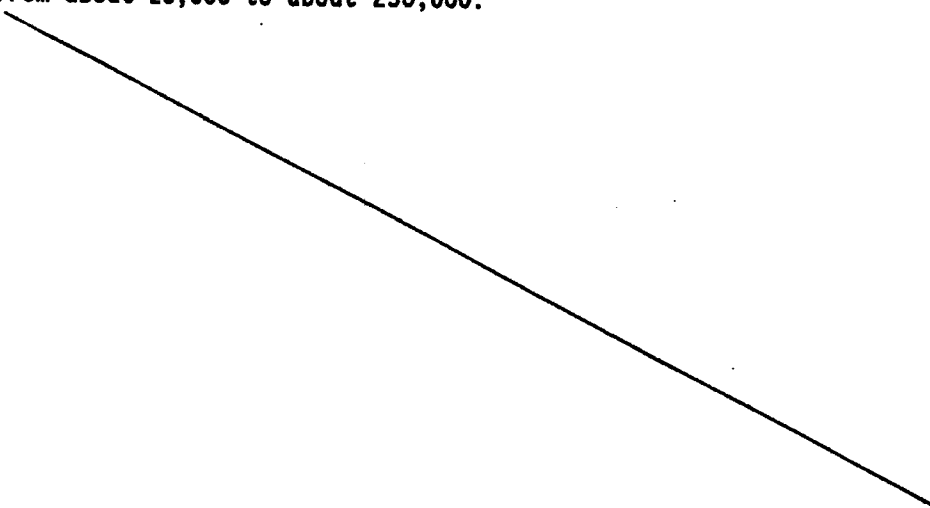
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preferably from about 100,000 to about 850,000, and most preferably from about 125,000 to about 750,000.

Alternatively, the copolymers of the present invention can also be represented by the formula



wherein A and B are as described herein, and where a is an integer of about 100 or greater, preferably a is an integer from about 100 to about 3000, more preferably from about 250 to about 2000, and most preferably from about 350 to about 1500, and b is an integer of about 2 or greater, preferably from about 2 to about 50, more preferably from about 2 to about 20, and most preferably from about 2 to about 10. In this formula, it is expressly intended that even though ranges are provided for the subscripts a and b, these subscripts are not intended to strictly limit the polymers herein so long as the physical propoerties of the polymers are achieved. When the copolymers herein are described by the formula disclosed in this paragraph it has been found useful to describe the copolymers by their number average molecule weights. In general, the number average molecular weight is less than about 2,500,000, more generally less than about 1,500,000, and typically less than about 1,000,000. Preferably, the number average molecular weight is from about 15,000 to about 1,000,000, more preferably from about 20,000 to about 500,000, and most preferably from about 25,000 to about 250,000.



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5 By appropriate selection and combination of the particular A and B units and by the choice of specific relative ratios of the units well within the ability of one of ordinary skill in the art, the copolymers can be optimized for various physical properties such as solubility, T_g's, and the like, and for compatibility with other ingredients commonly used in hair care and skin care applications.

10 When the copolymers of the present invention are incorporated into hair and/or skin care compositions, the copolymers typically comprise from about 0.1% to about 25%, preferably from about 0.5% to about 20%, more preferably from about 1% to about 10%, and most preferably from about 2% to about 5% of the composition, although
15 higher or lower amounts can be used depending upon the particular application.

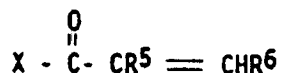
Monomer "A" Units

20 The "A" monomer unit is selected from polymerizable monomers, preferably ethylenically unsaturated monomers. Either a single A monomer or combinations of two or more A monomers can be utilized. For example, if two different A monomers are polymerized with a B macromonomer, the resulting copolymer could be described as a terpolymer. In either case, the monomers are selected to meet the requirements of the copolymer. By "polymerizable", as used
25 herein, is meant monomers that can be polymerized using any conventional synthetic techniques. Monomers that are polymerizable using conventional free radical initiated techniques are preferred. The term "ethylenically unsaturated" is used herein to mean monomers that contain at least one polymerizable carbon-carbon double bond (which can be mono-, di-, tri-, or
30 tetra-substituted).

The A monomer units of the copolymers of the present invention can comprise from about 40% to about 90%, more preferably from about 50% to about 85%, and most preferably from
35 about 60% to about 80%, by weight, of the copolymers.

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The ethylenically unsaturated A monomer units preferably can be described by the following formula



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wherein X is selected from the group consisting of -OH, -OM, -OR⁴, -NH₂, -NHR⁴, and -N(R⁴)₂; M is a cation selected from the group consisting of Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺, Zn⁺⁺, NH₄⁺, alkylammonium, dialkylammonium, trialkylammonium, and tetraalkylammonium; each R⁴ is independently selected from the group consisting of H, C₁-C₈ straight or branched chain alkyl, N,N-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl; and R⁵ and R⁶ are independently selected from the group consisting of H, C₁-C₈ straight or branched chain alkyl, methoxy, ethoxy, 2-hydroxyethoxy, 2-methoxyethyl, and 2-ethoxyethyl.

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Representative nonlimiting examples of monomers useful herein include acrylic acid and salts, esters, and amides thereof. The salts can be derived from any of the common nontoxic metal, ammonium, or substituted ammonium counter ions. The esters can be derived from C₁-40 straight chain, C₃-40 branched chain, or C₃-40 carbocyclic alcohols; from polyhydric alcohols having from about 2 to about 8 carbon atoms and from about 2 to about 8 hydroxy groups (nonlimiting examples of which include ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, glycerin, and 1,2,6-hexanetriol); from amino alcohols (nonlimiting examples of which include aminoethanol, dimethylaminoethanol, and diethylaminoethanol, and their quaternized derivatives); or from alcohol ethers (nonlimiting examples of which include methoxyethanol, and ethoxy ethanol). The amides can be unsubstituted, N-alkyl or N-alkylamino mono-substituted, or N,N-dialkyl or N,N-dialkylamino di-substituted, wherein the alkyl or alkylamino group can be derived from C₁-40 straight chain, C₃-40 branched chain, or C₃-40 carbocyclic moieties. Additionally, the alkylamino groups can be quaternized. Also useful as monomers are substituted acrylic acids and salts, esters, and amides

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thereof (wherein the substituents are on the two and three carbon positions of the acrylic acid and are independently selected from the group consisting of C₁₋₄ alkyl, -CN, -COOH (e.g., methacrylic acid, ethacrylic acid, and 3-cyano acrylic acid). The salts, esters, and amides of these substituted acrylic acids can be defined as described above for the acrylic acid salts, esters, and amides. Other useful monomers include vinyl and allyl esters of C₁₋₄₀ straight chain, C₃₋₄₀ branched chain, or C₃₋₄₀ carbocyclic carboxylic acids; vinyl and allyl halides (e.g., vinyl chloride and allyl chloride); vinyl and allyl substituted heterocyclic compounds (e.g., vinyl pyrridine and allyl pyridine); vinylidene chloride; and hydrocarbons having at least one carbon-carbon double bond (e.g., styrene, alpha-methylstyrene, t-butylstyrene, butadiene, isoprene, cyclohexadiene, ethylene, propylene, 1-butene, 2-butene, isobutylene, vinyl toluene); and mixtures thereof.

Preferred A monomers useful herein include those selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, methyl acrylate, ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, iso-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, decyl methacrylate, methyl ethacrylate, ethyl ethacrylate, n-butyl ethacrylate, iso-butyl ethacrylate, t-butyl ethacrylate, 2-ethylhexyl ethacrylate, decyl ethacrylate, 2,3-dihydroxypropyl acrylate, 2,3-dihydroxypropyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, hydroxypropyl methacrylate, glyceryl monoacrylate, glyceryl monomethacrylate, acrylamide, methacrylamide, ethacrylamide, N-methyl acrylamide, N,N-dimethyl acrylamide, N,N-dimethyl methacrylamide, N-ethylacrylamide, N-isopropyl acrylamide, N-butyl acrylamide, N-t-butyl acrylamide, N,N-di-n-butylacrylamide, N,N-diethylacrylamide, N-octyl acrylamide, N-octadecyl acrylamide, N-phenyl acrylamide, N-methyl methacrylamide,

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N-ethylmethacrylamide, N-dodecylmethacrylamide,
 N,N-dimethylaminoethyl acrylamide, quaternized
 N,N-dimethylaminoethyl acrylamide, N,N-dimethylaminoethyl
 methacrylamide, quaternized N,N-dimethylaminoethyl methacrylamide,
 5 N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl
 methacrylate, quaternized N,N-dimethylaminoethyl acrylate,
 quaternized N,N-dimethylaminoethyl methacrylate, 2-hydroxyethyl
 acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl ethacrylate,
 glyceryl acrylate, 2-methoxyethyl acrylate, 2-methoxyethyl
 10 methacrylate, 2-methoxyethyl ethacrylate, 2-ethoxyethyl acrylate,
 2-ethoxyethyl methacrylate, 2-ethoxyethyl ethacrylate, maleic
 acid, maleic anhydride and its half esters, crotonic acid,
 itaconic acid, angelic acid, diallyldimethyl ammonium chloride,
 vinyl pyrrolidone, methyl vinyl ether, methyl vinyl ketone, male-
 15 imide, vinyl pyridine, vinyl imidazole, vinyl furan, styrene
 sulfonate, allyl alcohol, vinyl alcohol, vinyl caprolactam, and
 mixtures thereof.

More preferred A monomers are those selected from the group
 consisting of methyl acrylate, methyl methacrylate, methyl
 20 ethacrylate, ethyl acrylate, ethyl methacrylate, ethyl
 ethacrylate, n-butyl acrylate, n-butyl methacrylate, n-butyl
 ethacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate,
 2-ethylhexyl ethacrylate, N-octyl acrylamide, 2-methoxyethyl
 acrylate, 2-hydroxyethyl acrylate, N,N-dimethylaminoethyl
 25 acrylate, and mixtures thereof.

Most preferred A monomers are those selected from the group
 consisting of n-butyl acrylate, 2-ethylhexyl acrylate, N-octyl
 acrylamide, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate,
 N,N-dimethylaminoethyl acrylate, and mixtures thereof.

30 Hydrophilic "B" Macromonomer Units

A macromonomer is a large monomer unit, i.e. a macromolecular
 monomer, which can be further polymerized with itself, with other
 conventional monomers, or with other macromonomers. The term
 "macromonomer" is one that is familiar to the polymer chemist of
 35 ordinary skill in the art. The hydrophilic "B" macromonomer units

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of the present invention are very large monomer building blocks which can be formed from the polymerization of smaller monomer units. The B macromonomers encompass a wide variety of structures and are copolymerizable with the A monomer. Either a
5 single B macromonomer or combinations of two or more B macromonomers can be utilized. In either case, the macromonomers are selected to meet the requirements of the copolymer.

The hydrophilic B macromonomers comprise from about 10% to about 60%, more preferably from about 15% to about 50%, and most
10 preferably from about 20% to about 40%, by weight of the copolymers.

By the term "copolymerizable" as used herein is meant B macromonomers that can be reacted with the A monomer in a polymerization reaction using any conventional synthetic
15 techniques. "Copolymerization" is a term of art used to refer to the simultaneous polymerization of two or more different monomers. In the present invention, B macromonomers that are copolymerizable with A monomers using conventional free radical initiated techniques are preferred. By the term "hydrophilic" as used
20 herein is meant B macromonomers that are soluble in or have an affinity for water and/or other polar, water-soluble solvent materials (e.g., methanol, ethanol, propanol, isopropanol and the like). "Hydrophilic" is also a term of art used to described a substance having a strong tendency to absorb water which results
25 in the swelling, solubilization, or dispersion of the substance in water. Without being limited by theory, the hydrophilic B macromonomer units are believed to contribute to the overall water or alcohol soluble or dispersible properties of the copolymers.

B macromonomers that are useful herein contain an
30 ethylenically unsaturated moiety that is copolymerizable with the A monomer. The term "ethylenically unsaturated" is used herein to mean B macromonomers that contain at least one carbon-carbon double bond (which can be mono-, di-, tri-, or tetra-substituted). Typically, the preferred B macromonomers are those that are
35 endcapped with the ethylenically unsaturated moiety. By

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"endcapped" as used herein is meant that the ethylenically unsaturated moiety is at or near a terminal position of the macromonomer. However, this definition of "endcapped" is not intended to limit the macromonomer to only those macromonomers which terminate in a carbon-carbon double bond (whether mono-, di-, tri-, or tetra-substituted).

The hydrophilic B macromonomers of the present invention can be synthesized utilizing a variety of standard synthetic procedures familiar to the polymer chemist of ordinary skill in the art. Furthermore, these macromonomers can be synthesized starting from commercially available polymers. Typically the weight average molecular weight of the macromonomer is from about 1000 to about 200,000, more preferably from 1500 to about 30,000, and most preferably from about 2000 to about 25,000.

For example, the hydrophilic B macromonomers can be synthesized by the polymerization (acid, base, free radical, or auto-initiated) of a hydrophilic monomer to form a polymer which is subsequently reacted with or "endcapped" with a structural unit E, containing the ethylenically unsaturated moiety. Alternatively, the B macromonomers can be synthesized starting with commercially available hydrophilic polymers which are "endcapped" with the structural unit E. In yet another alternative, the B macromonomer can be synthesized by starting with the structural unit E, and polymerizing onto it the desired hydrophilic monomer units. It is to be understood that in this third alternative, the ethylenically unsaturated moiety of the E unit is not consumed in the synthesis but its integrity is preserved for subsequent copolymerization of the B macromonomer with the A monomer units. All of the synthetic alternatives are merely illustrative in that any other suitable synthetic procedures can be utilized to prepare the B macromonomers and copolymers of the present invention.

The B macromonomers can be described by the following formula



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5 X is a hydrophilic monomer unit, and m is an integer from about 10 to about 2000, preferably from about 15 to about 300, and more preferably from about 20 to about 250, so that the macromonomer meets the weight average molecular weight requirements set forth above. Preferred is when X is a hydrophilic monomer unit selected from the group consisting of oxazolines, N-alkyloxazolines, alkylene glycols, N-vinylpyrrolidones, N-allylpyrrolidones, vinylpyridines, allylpyridines, vinylcaprolactams, allylcaprolactams, 10 vinylimidazoles, allylimidazoles, vinylfurans, allylfurans, vinyltetrahydrofurans, allyltetrahydrofurans, and mixtures thereof. More preferred is wherein X is a monomer unit selected from the group consisting of N-alkyloxazolines, alkylene glycols, and mixtures thereof. Most preferred is wherein X is a monomer unit selected from N-alkyloxazolines.

15 E is a structural unit containing the ethylenically unsaturated moiety or "endcapping" group. Preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, styryl, 3-vinylbenzyl, 4-vinylbenzyl, 20 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, isoprenyl, cyclohexyl, cyclopentyl, and mixtures thereof. More preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 25 1-propenyl, isobutenyl, and mixtures thereof. Most preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, and mixtures thereof.

30 I is an optionally present chemical moiety. In other words, n is an integer selected from zero and one. Without being limited by theory, I can be derived from a chemical initiator or solvent used in the synthesis of the B macromonomer. Nonlimiting examples of such initiators from which I can be derived include hydrogen ion, hydrogen radical, hydride ion, hydroxide ion, hydroxyl radical, peroxide radical, peroxide anion, C1-20 carbocations, 35

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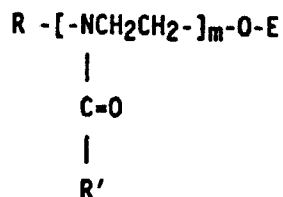
5 C1-20 carbanions, C1-20 carbon radicals, C1-20 aliphatic and aromatic alkoxy anions, ammonium ion, and substituted ammonium ions (e.g., C1-20 alkyl and C1-20 alkoxy substituted). I can be derived from any useful solvent, nonlimiting examples of which include water, methanol ethanol, propanol, isopropanol, acetone, hexane, dichloromethane, chloroform, benzene, and toluene. Nonlimiting examples of I include chemical moieties selected from the group consisting of H, C1-C6 alkyl, phenyl, 4-methylphenyl, and benzyl; preferably H, methyl, ethyl, and phenyl; and more preferably H, methyl, and ethyl.

10 Representative examples of classes of endcapped B macromonomers useful herein include those selected from the group consisting of endcapped poly(N-alkyloxazolines), endcapped polyalkylene glycol monoalkyl ethers, endcapped poly(N-vinylpyrrolidones), endcapped poly(N-allylpyrrolidones), endcapped polyvinylpyridines, endcapped polyallylpyridines, endcapped polyvinylcaprolactams, endcapped polyallylcaprolactams, endcapped polyvinylimidazoles, endcapped polyallylimidazoles, endcapped polyvinylfurans, endcapped polyvinyltetrahydrofurans, endcapped polyallylfurans, endcapped polyacrylic acids, endcapped polymethacrylic acids, endcapped polyallyltetrahydrofurans, and mixtures thereof.

20 Preferred are macromonomers selected from the group consisting of endcapped poly(N-alkyloxazolines), endcapped polyalkylene glycol monoalkyl ethers, and mixtures thereof.

25 More preferred are endcapped poly(N-alkyloxazoline) macromonomers.

30 Examples of endcapped poly(N-alkyloxazoline) macromonomers are those having the following chemical formula:

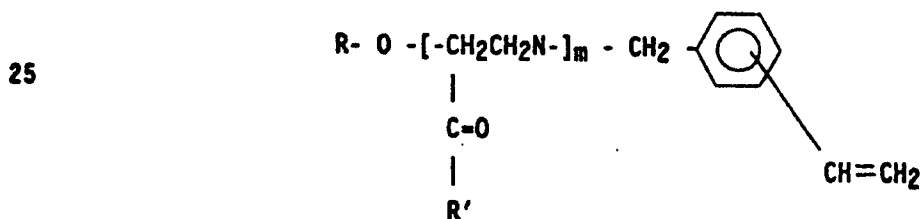


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wherein R and R' are independently selected from H or C₁₋₈ straight or branched chain alkyl, more preferably R and R' are independently selected from H, methyl, or ethyl; and most preferably R is methyl and R' is ethyl. E is a copolymerizable, ethylenically unsaturated moiety (i.e. the endcapping moiety). Preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, styryl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, isoprenyl, cyclohexyl, cyclopentyl, and mixtures thereof. More preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, and mixtures thereof. Most preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, styryl, 3-vinylbenzyl, 4-vinylbenzyl, and mixtures thereof. In the above structure m is preferably an integer from about 10 to about 2000, more preferably from about 15 to about 300, and most preferably from about 20 to about 250.

Alternatively, other examples of endcapped poly(N-alkyloxazoline) macromonomers are those having the following chemical formula:



wherein R and R' are independently selected from the group consisting of H or C₁₋₈ straight or branched chain alkyl, more preferably R and R' are independently selected from H, methyl, or ethyl; and most preferably R is H and R' is ethyl. In the above structure m is an integer from about 10 to about 2000, more

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preferably from about 15 to about 300, and most preferably from about 20 to about 250.

Highly preferred examples of endcapped poly(N-alkyloxazoline) macromonomers useful herein include acryloyl endcapped poly(2-ethyl oxazoline), methacryloyl endcapped poly(2-ethyl oxazoline), styryl endcapped poly(2-ethyloxazoline), acryloyl endcapped poly(2-methyl oxazoline), methacryloyl endcapped poly(2-methyl oxazoline), 3-vinylbenzoyl endcapped poly(2-methyloxazoline), 4-vinylbenzoyl endcapped poly(2-methyloxazoline), and mixtures thereof.

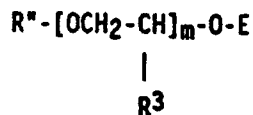
The endcapped poly(N-alkyloxazoline) macromonomers can be synthesized using standard synthetic procedures which involve polymerizing, usually under acid-catalyzed conditions, an N-alkyloxazoline to yield a poly(N-alkyloxazoline) alcohol. This alcohol can then be subsequently endcapped, employing standard reaction procedures, with the desired ethylenically unsaturated moiety using a reactive or activated form of an endcapping group. Suitable activated endcapping groups include vinyl, allyl, 1-propenyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, and 4-vinylbenzoyl halides (e.g. chlorides, bromides, and iodides), and the acid chlorides and bromides derived from acrylic acid, methacrylic acid, and ethacrylic acid. See, e.g., S.I. Shoda et al., "Synthesis and Surfactant Property of Copolymers Having a Poly(2-Oxazoline) Graft Chain", Journal of Polymer Science: Part A: Polymer Chemistry, vol. 30, pp. 1489-1494 (1992); T. Saegusa et al., "Macromolecular Engineering on the Basis of the Polymerization of 2-Oxazolines, Makromol. Chem., Macromol. Symp., vol. 51, pp. 1-10 (1991); S. Kobayashi et al., Macromolecules, vol. 22, pp. 2878-2884 (1989), and U.S. Patent No. 4,011,376, to Tomalia et al., issued March 8, 1977; and U.S. Patent No. 3,786,116, to Milkovich et al., issued January 15, 1974; all of which are incorporated herein by reference.

Alternatively the polyoxazoline macromonomers can be synthesized by polymerizing the monomers onto an appropriate endcapping group. For example, the vinyl benzyl endcapped

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polyoxazolines can be prepared by polymerizing 2-ethyl-2-oxazoline onto a mixture of 3-vinylbenzyl and 4-benzylchlorides. See EXAMPLE III.

Also highly useful herein are endcapped polyalkylene glycol monoalkyl ether macromonomers corresponding to the following general chemical formula



wherein R^n is selected from C1-C40 straight or branched chain alkyl, more preferably from C1-C8 straight or branched chain alkyl, most preferably from C1-C4 straight or branched chain alkyl, and most preferably methyl; R^3 is selected from hydrogen, methyl, ethyl, or n-propyl, more preferably from hydrogen or methyl, most preferably from H. E is a copolymerizable, ethylenically unsaturated moiety (i.e. the endcapping moiety). Preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, styryl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, isoprenyl, cyclohexyl, cyclopentyl, and mixtures thereof. More preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, and mixtures thereof. Most preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, styryl, 3-vinylbenzyl, 4-vinylbenzyl, and mixtures thereof. In the above structure, m is as described previously, wherein m is preferably an integer from about 20 to about 2000, more preferably from about 30 to about 750, and most preferably from about 40 to about 500. It is to be understood that in the above structure, that when R^3 is other than hydrogen that various isomers of the resulting macromonomer are possible depending upon the orientation of the individual glycol moieties. Therefore, the structure depicted above for these endcapped polyalkylene glycol

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monoalkyl ethers is a general one that is not intended to limit these materials to any one particular isomeric structure.

5 Highly preferred examples of endcapped polyalkylene glycol monoalkyl ethers useful herein include acryloyl endcapped polyethylene glycol monomethyl ether, 3-vinylbenzoyl endcapped polyethylene glycol monomethyl ether, 4-vinylbenzoyl endcapped polyethylene glycol monomethyl ether, methacryloyl endcapped polyethylene glycol monomethyl ether, and mixtures thereof.

10 The endcapped polyalkylene glycol monoalkyl ethers can be synthesized from the polyalkylene glycol monoalkyl ether and the reactive or activated form of an endcapping group employing standard reaction procedures. Suitable activated endcapping groups include vinyl, allyl, 3-vinylbenzoyl, and 4-vinylbenzoyl halides (e.g. chlorides, bromides, and iodides), and the acid
15 chlorides and bromides derived from acrylic acid, methacrylic acid, and ethacrylic acid. The polyalkylene glycol monoalkyl ether can be synthesized from the corresponding polyalkylene glycol using any of the alkylating agents well known in the art (e.g., methyl iodide, methyl bromide, diazomethane, methyl sulfate, ethyl iodide). Polyethylene glycols of various molecular weight ranges, as well as their methyl ethers are commercially available from Aldrich Chemical Company and Union Carbide Corporation. Alternatively, the polyalkylene glycols can be
20 synthesized from the corresponding alkylene oxides and alkylene glycols using standard synthetic procedures (e.g., the acid or base catalyzed polymerization of alkylene oxides).

Synthesis of the Copolymers

30 In general, the copolymers can be made by free radical polymerization of the A monomers with the B macromonomers. It is not intended to necessarily exclude from this invention any copolymers made by means other than free radical polymerization, so long as the product has the desired physical properties. The copolymers herein contain randomly repeating monomer units and macromonomer units.

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The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. The desired monomers and macromonomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Typical monomer and macromonomer loadings are from about 10% to about 50%, on a weight basis. Undesired terminators, especially oxygen, can be removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Nonlimiting examples of suitable initiators include those selected from the group consisting of azo initiators, peroxide initiators, redox initiators, and photochemical initiators. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The copolymer can be further purified, as needed utilizing a variety of techniques including filtration, extraction, trituration, membrane separation, gel permeation chromatography, and like.

There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, reaction loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers and macromonomer used, because different monomers and macromonomers have different solubilities and different reactivities to a specific initiator.

The copolymers of the present invention can also be synthesized by first preparing the backbone from the polymerization of suitable monomers, followed by further polymerization of the backbone with suitable hydrophilic monomers

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to form the polymeric side chains. This alternative procedure for synthesizing the copolymers herein is illustrated in EXAMPLE VIII below.

5 Analysis of the copolymer reaction product and the extracted materials, and the purified copolymer can be performed by conventional analysis techniques known in the art. These include, for example, nuclear magnetic resonance (NMR), infrared molecular spectroscopies, gel permeation/size exclusion chromatography, membrane osmometry, and atomic absorption and emission
10 spectroscopies.

Hair Care and Topical Skin Care Compositions

The copolymers of the present invention can be formulated into a wide variety of product types, including mousses, gels, lotions, tonics, sprays, shampoos, conditioners, rinses, hand and
15 body lotions, facial moisturizers, sunscreens, anti-acne preparations, topical analgesics, mascaras, and the like. The carriers and additional components required to formulate such products vary with product type and can be routinely chosen by one skilled in the art. The following is a description of some of
20 these carriers and additional components.

Carriers

Hair Care Compositions

The hair care compositions of the present invention can comprise a carrier, or a mixture of such carriers, which are
25 suitable for application to the hair. The carriers are present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%, more preferably from about 10.0% to about 98.0%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or
30 negatively affect the aesthetics of hair or cause irritation to the underlying skin.

Carriers suitable for use with hair care compositions of the present invention include, for example, those used in the formulation of hair sprays, mousses, tonics, gels, shampoos,
35 conditioners, and rinses. The choice of appropriate carrier will

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also depend on the particular copolymer to be used, and whether the product formulated is meant to be left on the surface to which it is applied (e.g., hair spray, mousse, tonic, or gel) or rinsed off after use (e.g., shampoo, conditioner, rinse).

5 The carriers used herein can include a wide range of components conventionally used in hair care compositions. The carriers can contain a solvent to dissolve or disperse the particular copolymer being used, with water, the C1-C6 alcohols, and mixtures thereof being preferred; and water, methanol, 10 ethanol, isopropanol, and mixtures thereof being more preferred. The carriers can also contain a wide variety of additional materials including, but not limited to acetone, hydrocarbons (such as isobutane, hexane, decene), halogenated hydrocarbons (such as Freons), linalool, esters (such as ethyl acetate, dibutyl 15 phthalate), and volatile silicon derivatives (especially siloxanes such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane, cyclomethicone, and dimethicone 20 having for example, a viscosity at 25°C of about 15 centipoise or less), and mixtures thereof. When the hair care composition is a hair spray, tonic, gel, or mousse the preferred solvents include water, ethanol, volatile silicone derivatives, and mixtures thereof. The solvents used in such mixtures may be miscible or 25 immiscible with each other. Mousses and aerosol hair sprays can also utilize any of the conventional propellants to deliver the material as a foam (in the case of a mousse) or as a fine, uniform spray (in the case of an aerosol hair spray). Examples of suitable propellants include materials such as trichloro- 30 fluoromethane, dichlorodifluoromethane, difluoroethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also utilize an emulsifying agent. Examples of suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. 35 Fluorosurfactants are especially preferred, particularly if the

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5 product is a hair spray composition and most especially if it is a spray composition having relatively low levels of volatile organic solvents, such as alcohols, and relatively high levels of water (e.g., in excess of about 10%, by weight water). If such an emulsifying agent is used, it is preferably present at a level of from about 0.01% to about 7.5% of the composition. The level of propellant can be adjusted as desired but is generally from about 3% to about 30% of mousse compositions and from about 15% to about 50% of the aerosol hair spray compositions.

10 Suitable spray containers are well known in the art and include conventional, non-aerosol pump sprays i.e., "atomizers," aerosol containers or cans having propellant, as described above, and also pump aerosol containers utilizing compressed air as the propellant. Pump aerosol containers are disclosed, for example, 15 in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and also in U.S. Serial No. 07/839,648, Gosselin, Lund, Sojka, and Lefebvre, filed February 21, 1992, "Consumer Product Package Incorporating A Spray Device Utilizing Large Diameter Bubbles. 20 Pump aerosols hair sprays using compressed air are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY® hair sprays.

25 Where the hair care compositions are conditioners and rinses the carrier can include a wide variety of conditioning materials. Where the hair care compositions are shampoos, the carrier can include surfactants, suspending agents, thickeners etc. Various additional components useful in hair care compositions are described in U.S. Patent No. 5,106,609, to Bolich, Jr. et al., issued April 21, 1992; and U.S. Patent No. 4,387,090, to Bolich, Jr. issued June 7, 1983; which are incorporated by reference 30 herein. Some of these additional components are described below.

Topical Skin Care Compositions

35 The topical cosmetic and pharmaceutical compositions of the present invention can comprise a carrier. The carrier should be "cosmetically and/or pharmaceutically acceptable", which means

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that the carrier is suitable for topical application to the skin, has good aesthetic properties, is compatible with the copolymers of the present invention and any other components, and will not cause any untoward safety or toxicity concerns.

5 The carrier can be in a wide variety of forms. For example, emulsion carriers, including, but not limited to, oil-in-water, water-in-oil, water-in-oil-in-water, and oil-in-water-in-silicone emulsions, are useful herein. These emulsions can cover a broad
10 range of viscosities, e.g., from about 100 cps to about 200,000 cps. These emulsions can also be delivered in the form of sprays using either mechanical pump containers or pressurized aerosol containers using conventional propellants. These carriers can also be delivered in the form of a mousse. Other suitable topical
15 carriers include anhydrous liquid solvents such as oils, alcohols, and silicones (e.g., mineral oil, ethanol, isopropanol, dimethicone, cyclomethicone, and the like); aqueous-based single phase liquid solvents (e.g., hydro-alcoholic solvent systems); and thickened versions of these anhydrous and aqueous-based single
20 phase solvents (e.g., where the viscosity of the solvent has been increased to form a solid or semi-solid by the addition of appropriate gums, resins, waxes, polymers, salts, and the like). Examples of topical carrier systems useful in the present invention are described in the following four references all of
25 which are incorporated herein by reference in their entirety: "Sun Products Formulary" Cosmetics & Toiletries, vol. 105, pp. 122-139 (December 1990); "Sun Products Formulary", Cosmetics & Toiletries, vol. 102, pp. 117-136 (March 1987); U.S. Patent No. 4,960,764 to Figueroa et al., issued October 2, 1990; and U.S. Patent No. 4,254,105 to Fukuda et al., issued March 3, 1981.

30 The carriers of the skin care compositions can comprise from about 50% to about 99% by weight of the compositions of the present invention, preferably from about 75% to about 99%, and most preferably from about 85% to about 95%.

35 Preferred cosmetically and/or pharmaceutically acceptable topical carriers include hydro-alcoholic systems and oil-in-water

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emulsions. When the carrier is a hydro-alcoholic system, the carrier can comprise from about 1% to about 99% of ethanol, isopropanol, or mixtures thereof, and from about 1% to about 99% of water. More preferred is a carrier comprising from about 5% to about 60% of ethanol, isopropanol, or mixtures thereof, and from about 40% to about 95% of water. Especially preferred is a carrier comprising from about 20% to about 50% of ethanol, isopropanol, or mixtures thereof, and from about 50% to about 80% of water. When the carrier is an oil-in-water emulsion, the carrier can include any of the common excipient ingredients for preparing these emulsions. Additional components useful in formulating these topical compositions are further described below.

Additional Components

A wide variety of additional components can be employed in the hair care and topical skin compositions herein. Non-limiting examples include the following:

Pharmaceutical Actives

The compositions of the present invention, especially the topical skin care compositions, can comprise a safe and effective amount of a pharmaceutical active. The phrase "safe and effective amount", as used herein, means an amount of an active high enough to significantly or positively modify the condition to be treated, but low enough to avoid serious side effects (at a reasonable benefit/risk ratio); within the scope of sound medical judgement. A safe and effective amount of the pharmaceutical active will vary with the specific active, the ability of the composition to penetrate the active through the skin, the amount of composition to be applied, the particular condition being treated, the age and physical condition of the patient being treated, the severity of the condition, the duration of the treatment, the nature of concurrent therapy, and like factors.

The pharmaceutical actives which can be used in the compositions of the present invention preferably comprise from about 0.1% to about 20% by weight of the compositions, more

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preferably from about 0.1% to about 10%, and most preferably from about 0.1% to about 5%. Mixtures of pharmaceutical actives may also be used.

5 Nonlimiting examples of pharmaceutical actives can include the following:

Useful pharmaceutical actives in the compositions of the present invention include anti-acne drugs. Anti-acne drugs preferred for use in the present invention include the
10 keratolytics such as salicylic acid, sulfur, lactic acid, glycolic, pyruvic acid, urea, resorcinol, and N-acetylcysteine; retinoids such as retinoic acid and its derivatives (e.g., cis and trans); antibiotics and antimicrobials such as benzoyl peroxide, octopirox, erythromycin, zinc, tetracyclin, triclosan, azelaic acid and its derivatives, phenoxy ethanol and phenoxy propanol,
15 ethylacetate, clindamycin and meclocycline; sebastats such as flavinoids; alpha and beta hydroxy acids; and bile salts such as scymnol sulfate and its derivatives, deoxycholate, and cholate. Preferred for use herein is salicylic acid.

Useful pharmaceutical actives in the compositions of the present invention include non-steroidal anti-inflammatory drugs (NSAIDS). The NSAIDS can be selected from the following
20 categories: propionic acid derivatives; acetic acid derivatives; fenamic acid derivatives; biphenylcarboxylic acid derivatives; and oxicams. All of these NSAIDS are fully described in the U.S. Patent 4,985,459 to Sunshine et al., issued January 15, 1991, incorporated by reference herein. Most preferred are the propionic NSAIDS including but not limited to aspirin, acetaminophen, ibuprofen, naproxen, benoxaprofen, flurbiprofen, fenoprofen, fenbufen, ketoprofen, indoprofen, piroprofen,
25 carprofen, oxaprozin, pranoprofen, miroprofen, tiroxaprofen, suprofen, alminoprofen, tiaprofenic acid, fluprofen and bucloxic acid. Also useful are the steroidal anti-inflammatory drugs including hydrocortisone and the like.

Useful pharmaceutical actives in the compositions of the present invention include antipruritic drugs. Antipruritic drugs
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preferred for inclusion in compositions of the present invention include pharmaceutically-acceptable salts of methdilazine and trimeprazine.

5 Useful pharmaceutical actives in the compositions of the present invention include include anesthetic drugs. Anesthetic drugs preferred for inclusion in compositions of the present invention include pharmaceutically-acceptable salts of lidocaine, bupivacaine, chlorprocaine, dibucaine, etidocaine, mepivacaine, tetracaine, dyclonine, hexylcaine, procaine, cocaine, ketamine, 10 pramoxine and phenol.

Useful pharmaceutical actives in the compositions of the present invention include antimicrobial drugs (antibacterial, antifungal, antiprotozoal and antiviral drugs). Antimicrobial drugs preferred for inclusion in compositions of the present invention include pharmaceutically-acceptable salts of β -lactam 15 drugs, quinolone drugs, ciprofloxacin, norfloxacin, tetracycline, erythromycin, amikacin, triclosan, doxycycline, capreomycin, chlorhexidine, chlortetracycline, oxytetracycline, clindamycin, ethambutol, metronidazole, pentamidine, gentamicin, kanamycin, lineomycin, methacycline, methenamine, minocycline, neomycin, 20 netilmicin, paromomycin, streptomycin, tobramycin, miconazole and amanfadine. Antimicrobial drugs preferred for inclusion in compositions of the present invention include tetracycline hydrochloride, erythromycin estolate, erythromycin stearate 25 (salt), amikacin sulfate, doxycycline hydrochloride, capreomycin sulfate, chlorhexidine gluconate, chlorhexidine hydrochloride, chlortetracycline hydrochloride, oxytetracycline hydrochloride, clindamycin hydrochloride, ethambutol hydrochloride, metronidazole hydrochloride, pentamidine hydrochloride, gentamicin sulfate, 30 kanamycin sulfate, lineomycin hydrochloride, methacycline hydrochloride, methenamine hippurate, methenamine mandelate, minocycline hydrochloride, neomycin sulfate, netilmicin sulfate, paromomycin sulfate, streptomycin sulfate, tobramycin sulfate, miconazole hydrochloride, amanfadine hydrochloride, amanfadine 35

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sulfate, triclosan, octopirox, parachlorometa xlenol, nystatin, tolnaftate and clotrimazole.

Also useful herein are sunscreens agents. A wide variety of sunscreens agents are described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 5,073,372, to Turner et al., issued December 17, 1991; U.S. Patent No. 5,073,371, to Turner et al. issued December 17, 1991; and Segarin, et al., at Chapter VIII, pages 189 et seq., of Cosmetics Science and Technology, all of which are incorporated herein by reference in their entirety.

Preferred among those sunscreens which are useful in the compositions of the instant invention are those selected from the group consisting of 2-ethylhexyl p-methoxycinnamate, 2-ethylhexyl N,N-dimethyl-p-aminobenzoate, p-aminobenzoic acid, 2-phenylbenzimidazole-5-sulfonic acid, octocrylene, oxybenzone, homomenthyl salicylate, octyl salicylate, 4,4'-methoxy-t-butyl dibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-benzylidene camphor, 3-(4-methylbenzylidene) camphor, titanium dioxide, zinc oxide, silica, iron oxide, and mixtures thereof.

Still other useful sunscreens are those disclosed in U.S. Patent No. 4,937,370, to Sabatelli, issued June 26, 1990; and U.S. Patent No. 4,999,186, to Sabatelli et al., issued March 12, 1991; these two references are incorporated by reference herein in their entirety. The sunscreens agents disclosed therein have, in a single molecule, two distinct chromophore moieties which exhibit different ultra-violet radiation absorption spectra. One of the chromophore moieties absorbs predominantly in the UVB radiation range and the other absorbs strongly in the UVA radiation range. These sunscreens agents provide higher efficacy, broader UV absorption, lower skin penetration and longer lasting efficacy relative to conventional sunscreens. Especially preferred examples of these sunscreens include those selected from the group consisting of 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester of 2,4-dihydroxybenzophenone, 4-N,N-(2-ethylhexyl)methylaminobenzoic

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acid ester with 4-hydroxydibenzoylmethane, 4-N,N-(2-ethylhexyl)-methylaminobenzoic acid ester of 2-hydroxy-4-(2-hydroxyethoxy)benzophenone, 4-N,N-(2-ethylhexyl)-methylaminobenzoic acid ester of 4-(2-hydroxyethoxy)dibenzoylmethane, and mixtures thereof.

5 Generally, the sunscreens can comprise from about 0.5% to about 20% of the compositions useful herein. Exact amounts will vary depending upon the sunscreen chosen and the desired Sun Protection Factor (SPF). SPF is a commonly used measure of photoprotection of a sunscreen against erythema. See Federal
10 Register, Vol. 43, No. 166, pp. 38206-38269, August 25, 1978, which is incorporated herein by reference in its entirety.

Also useful in the present invention are sunless tanning agents including dihydroxyacetone, glyceraldehyde, indoles and their derivatives, and the like. These sunless tanning agents may
15 also be used in combination with the sunscreen agents.

Other useful actives include skin bleaching (or lightening) agents including but not limited to hydroquinone, ascorbic acid, kojic acid and sodium metabisulfite.

Other useful actives which are especially useful for hair care compositions include anti-dandruff actives such as zinc
20 pyrithione, octopirox, selenium disulfide, sulfur, coal tar, and the like.

Conditioners

Conditioning agents useful herein, and especially useful for hair care compositions, include hydrocarbons, silicone fluids, and
25 cationic materials.

The hydrocarbons can be either straight or branched chain and can contain from about 10 to about 16, preferably from about 12 to about 16 carbon atoms. Examples of suitable hydrocarbons are
30 decane, dodecane, tetradecane, tridecane, and mixtures thereof.

Silicone conditioning agents useful herein can include either cyclic or linear polydimethylsiloxanes, phenyl and alkyl phenyl silicones, and silicone copolyols. The linear volatile silicones generally have viscosities of less than about 5 centistokes at
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250C, while the cyclic materials have viscosities less than about 10 centistokes.

Cationic conditioning agents useful herein can include quaternary ammonium salts or the salts of fatty amines. Preferred quaternary ammonium salts are dialkyl dimethyl ammonium chlorides, wherein the alkyl groups have from 12 to 22 carbon atoms and are derived from long-chain fatty acids. Representative examples of quaternary ammonium salts include ditallow dimethyl ammonium chloride, ditallow dimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, and di(hydrogenated tallow) ammonium chloride. Other quaternary ammonium salts useful herein are dicationics such as tallow propane diammonium dichloride. Quaternary imidazolinium salts are also useful herein. Examples of such materials are those imidazolinium salts containing C12-22 alkyl groups such as 1-methyl-1-[(stearoylamide)ethyl]-2-heptadecyl-4,5-dihydroimidazolinium chloride, 1-methyl-1-[(palmitoylamide)ethyl]-2-octadecyl-4,5-dihydroimidazolinium chloride and 1-methyl-1-[(tallowamide)-ethyl]-2-tallow-imidazolinium methyl sulfate. Also useful herein are salts of fatty amines. Examples of such compounds include stearylamine hydrochloride, soyamine hydrochloride, and stearylamine formate. Useful conditioning agents are disclosed in U.S. Patent No. 4,387,090, to Bolich, issued June 7, 1983, which is incorporated by reference herein.

Humectants and Moisturizers

The compositions of the present invention can contain one or more humectant or moisturizing materials. A variety of these materials can be employed and each can be present at a level of from about 0.1% to about 20%, more preferably from about 1% to about 10% and most preferably from about 2% to about 5%. These materials include urea; guanidine; glycolic acid and glycolate salts (e.g. ammonium and quaternary alkyl ammonium); lactic acid and lactate salts (e.g. ammonium and quaternary alkyl ammonium); aloe vera in any of its variety of forms (e.g., aloe vera gel);

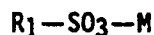
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polyhydroxy alcohols such as sorbitol, glycerol, hexanetriol, propylene glycol, butylene glycol, hexylene glycol and the like; polyethylene glycols; sugars and starches; sugar and starch derivatives (e.g., alkoxylated glucose); hyaluronic acid; 5 lactamide monoethanolamine; acetamide monoethanolamine; and mixtures thereof. Preferred humectants and moisturizers are glycerol, butylene glycol, hexylene glycol, and mixtures thereof.

Surfactants

10 The compositions of the present invention, especially the shampoo and conditioner compositions, can contain one or more surfactants. These surfactants are useful adjuncts for the carriers of the present compositions, and are not required for solubilizing or dispersing the copolymers of the present invention. For a shampoo, the level is preferably from about 15 10% to about 30%, preferably from 12% to about 25%, of the composition. For conditioners, the preferred level of surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants. A wide variety 20 of surfactants useful herein are disclosed in U.S. Patent No. 5,151,209, to Mc Call et al., issued September 29, 1992; U.S. Patent No. 5,151,210, to Steuri et al., issued September 29, 1992; and U.S. Patent No. 5,120,532, to Wells et al., issued June 9, 1992, all of which are incorporated by reference herein.

25 Nonlimiting examples of these surfactants include anionic surfactants such as alkyl and alkyl ether sulfates. These materials typically have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$, wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble 30 cation such as ammonium, sodium, potassium and triethanolamine. Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



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wherein R_1 is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Still other anionic synthetic surfactants include the class designated as succinamates, olefin sulfonates having about 12 to about 24 carbon atoms, and β -alkyloxy alkane sulfonates. Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's, Detergents and Emulsifiers, 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference.

Nonionic surfactants useful herein are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant. These nonionic surfactants can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature.

Cationic surfactants useful in compositions of the present invention are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the

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compositions of the present invention, the cationic surfactant is present at from about 0.05% to about 5%.

5 Zwitterionic surfactants are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha-carboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl 15 bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine, coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, 20 lauryl bis-(2-hydroxyethyl) sulfopropyl betaine, and amidobetaines and amidosulfobetaines (wherein the $\text{RCONH}(\text{CH}_2)_3$ radical is attached to the nitrogen atom of the betaine).

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly 25 described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, 30 or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylamino-propane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids 35 such as those produced according to the teaching of U.S. Patent

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2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.

Carboxylic Acid Copolymer Thickeners

5 Another component useful in the compositions herein is a carboxylic copolymer thickener. These crosslinked polymers contain one or more monomers derived from acrylic acid, substituted acrylic acids, and salts and esters of these acrylic acids and the substituted acrylic acids, wherein the crosslinking agent contains two or more carbon-carbon double bonds and is
10 derived from a polyhydric alcohol. The preferred polymers for use herein are of two general types. The first type of polymer is a crosslinked homopolymer of an acrylic acid monomer or derivative thereof (e.g., wherein the acrylic acid has substituents on the two and three carbon positions independently selected from the group consisting of C₁₋₄ alkyl, -CN, -COOH, and mixtures thereof).
15 The second type of polymer is a crosslinked copolymer having a first monomer selected from the group consisting of an acrylic acid monomer or derivative thereof (as just described in the previous sentence), a short chain alcohol (i.e. a C₁₋₄) acrylate ester monomer or derivative thereof (e.g., wherein the acrylic acid portion of the ester has substituents on the two and three carbon positions independently selected from the group consisting of C₁₋₄ alkyl, -CN, -COOH, and mixtures thereof), and mixtures thereof; and a second monomer which is a long chain alcohol (i.e. C₈₋₄₀) acrylate ester monomer or derivative thereof (e.g., wherein the acrylic acid portion of the ester has substituents on the two and three carbon positions independently selected from the group consisting of C₁₋₄ alkyl, -CN, -COOH, and mixtures thereof).
20 Combinations of these two types of polymers are also useful herein.
25
30

In the first type of crosslinked homopolymers the monomers are preferably selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, and mixtures thereof, with acrylic acid being most preferred. In the second type of
35 crosslinked copolymers the acrylic acid monomer or derivative

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thereof is preferably selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, and mixtures thereof, with acrylic acid, methacrylic acid, and mixtures thereof being most preferred. The short chain alcohol acrylate ester monomer or derivative thereof is preferably selected from the group consisting of C₁₋₄ alcohol acrylate esters, C₁₋₄ alcohol methacrylate esters, C₁₋₄ alcohol ethacrylate esters, and mixtures thereof, with the C₁₋₄ alcohol acrylate esters, C₁₋₄ alcohol methacrylate esters, and mixtures thereof, being most preferred. The long chain alcohol acrylate ester monomer is selected from C₈₋₄₀ alkyl acrylate esters, with C₁₀₋₃₀ alkyl acrylate esters being preferred.

The crosslinking agent in both of these types of polymers is a polyalkenyl polyether of a polyhydric alcohol containing more than one alkenyl ether group per molecule, wherein the parent polyhydric alcohol contains at least 3 carbon atoms and at least 3 hydroxyl groups. Preferred crosslinkers are those selected from the group consisting of allyl ethers of sucrose and allyl ethers of pentaerythritol, and mixtures thereof. These polymers useful in the present invention are more fully described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 4,509,949, to Huang et al., issued April 5, 1985; U.S. Patent No. 2,798,053, to Brown, issued July 2, 1957; which are incorporated by reference herein. See also, CTFA International Cosmetic Ingredient Dictionary, fourth edition, 1991, pp. 12 and 80; which are also incorporated herein by reference.

Examples of commercially available homopolymers of the first type useful herein include the carbomers, which are homopolymers of acrylic acid crosslinked with allyl ethers of sucrose or pentaerythritol. The carbomers are available as the Carbopol[®] 900 series from B.F. Goodrich. Examples of commercially available copolymers of the second type useful herein include copolymers of C₁₀₋₃₀ alkyl acrylates with one or more monomers of acrylic acid, methacrylic acid, or one of their short chain (i.e. C₁₋₄ alcohol) esters, wherein the crosslinking agent is an allyl ether of

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5 sucrose or pentaerythritol. These copolymers are known as acrylates/C10-30 alkyl acrylate crosspolymers and are commercially available as Carbopol^R 1342, Pemulen TR-1, and Pemulen TR-2, from B.F. Goodrich. In other words, examples of carboxylic acid
polymer thickeners useful herein are those selected from the group consisting of carbomers, acrylates/C10-C30 alkyl acrylate crosspolymers, and mixtures thereof.

10 The compositions of the present can comprise from about 0.025% to about 1%, more preferably from about 0.05% to about 0.75% and most preferably from about 0.10% to about 0.50% of the carboxylic acid polymer thickeners.

Emulsifiers

15 The compositions herein can contain various emulsifiers. These emulsifiers are useful for emulsifying the various carrier components of the compositions herein, and are not required for solubilizing or dispersing the copolymers of the present invention. Suitable emulsifiers can include any of a wide variety of nonionic, cationic, anionic, and zwitterionic emulsifiers disclosed in the prior patents and other references. See
20 McCutcheon's, Detergents and Emulsifiers, North American Edition (1986), published by Allured Publishing Corporation; U.S. Patent No. 5,011,681 to Ciotti et al., issued April 30, 1991; U.S. Patent No. 4,421,769 to Dixon et al., issued December 20, 1983; and U.S. Patent No. 3,755,560 to Dickert et al., issued August 28, 1973;
25 these four references are incorporated herein by reference in their entirety.

30 Suitable emulsifier types include esters of glycerin, esters of propylene glycol, fatty acid esters of polyethylene glycol, fatty acid esters of polypropylene glycol, esters of sorbitol, esters of sorbitan anhydrides, carboxylic acid copolymers, esters and ethers of glucose, ethoxylated ethers, ethoxylated alcohols, alkyl phosphates, polyoxyethylene fatty ether phosphates, fatty acid amides, acyl lactylates, soaps and mixtures thereof.

35 Suitable emulsifiers can include, but are not limited to, polyethylene glycol 20 sorbitan monolaurate (Polysorbate 20),

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polyethylene glycol 5 soya sterol, Steareth-20, Cetareth-20, PPG-2 methyl glucose ether distearate, Ceteth-10, Polysorbate 80, cetyl phosphate, potassium cetyl phosphate, diethanolamine cetyl phosphate, Polysorbate 60, glyceryl stearate, PEG-100 stearate, and mixtures thereof.

The emulsifiers can be used individually or as a mixture of two or more and can comprise from about 0.1% to about 10%, more preferably from about 1% to about 7%, and most preferably from about 1% to about 5% of the compositions of the present invention.

Emollients

The compositions useful in the methods of the present invention can also optionally comprise at least one emollient. Examples of suitable emollients include, but are not limited to, volatile and non-volatile silicone oils, highly branched hydrocarbons, and non-polar carboxylic acid and alcohol esters, and mixtures thereof. Emollients useful in the instant invention are further described in U.S. Patent No. 4,919,934, to Deckner et al., issued April 24 1990, which is incorporated herein by reference in its entirety.

The emollients can typically comprise in total from about 1% to about 50%, preferably from about 1% to about 25%, and more preferably from about 1% to about 10% by weight of the compositions useful in the present invention.

Additional Components

A variety of additional components can be incorporated into the compositions herein. Non-limiting examples of these additional components include vitamins and derivatives thereof (e.g., ascorbic acid, vitamin E, tocopheryl acetate, retinoic acid, retinol, retinoids, and the like); low pH thickening agents (e.g. polyacrylamide and C13-14 isoparaffin and laureth-7, available as Sepigel from Seppic Corporation; polyquaternium and mineral oil, available as Salcare SC92, from Allied Colloids; crosslinked methyl quaternized dimethylaminomethacrylate and mineral oil, available as Salcare SC95 from Allied Colloids; resins; gums and thickeners such as xanthan gum, carboxymethyl

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cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, alkyl-modified hydroxyalkyl celluloses (e.g. long chain alkyl modified hydroxyethyl celluloses such as cetyl hydroxyethylcellulose), and magnesium aluminum silicate; cationic polymers and thickeners (e.g., cationic guar gum derivatives such as guar hydroxypropyltrimonium chloride and hydroxypropyl guar hydroxypropyltrimonium chloride, available as the Jaguar C series from Rhone-Poulenc; polymers for aiding the film-forming properties and substantivity of the composition (such as a copolymer of eicosene and vinyl pyrrolidone, an example of which is available from GAF Chemical Corporation as Ganex^R V-220); suspending agents such as ethylene glycol distearate and the like; preservatives for maintaining the antimicrobial integrity of the compositions; skin penetration aids such as DMSO, 1-dodecylazacycloheptan-2-one (available as Azone from the Upjohn Co.) and the like; antioxidants; chelators and sequestrants; and aesthetic components such as fragrances, colorings, essential oils, skin sensates, astringents, skin soothing agents, skin healing agents and the like, nonlimiting examples of these aesthetic components include panthenol and derivatives (e.g. ethyl panthenol), pantothenic acid and its derivatives, clove oil, menthol, camphor, eucalyptus oil, eugenol, menthyl lactate, witch hazel distillate, allantoin, bisabolol, dipotassium glycyrrhizinate and the like.

Method of Using Hair and Skin Care Compositions

The hair care and skin care compositions of the present invention are used in conventional ways to provide the desired benefit appropriate to the product such as hair styling, holding, cleansing, conditioning and the like for hair care compositions and benefits such as moisturization, sun protection, anti-acne, anti-wrinkling, artificial tanning, analgesic, and other cosmetic and pharmaceutical benefits for skin care compositions. Such methods of use depend upon the type of composition employed but generally involve application of an effective amount of the product to the hair or skin, which may then be rinsed from the

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5 hair or skin (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, or gel products), or allowed to remain on the skin (as in the case of the skin care compositions). By "effective amount" is meant an amount sufficient to provide the benefit desired. Preferably, hair rinse, mousse, and gel products are applied to wet or damp hair prior to drying and styling of the hair. After such compositions are applied to the hair, the hair is dried and styled in the usual ways of the user. Hair sprays are typically applied to dry hair after it has already been dried and styled. Cosmetic and pharmaceutical topical skin care compositions are applied to and rubbed into the skin.

10 The following examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

20 EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention.

25 Ingredients are identified by chemical or CTFA name.

EXAMPLE I

Synthesis of Poly(2-ethyl-2-oxazoline) Alcohol

30 To a solution of 50 g (0.5044 mol) of 2-ethyl-2-oxazoline in 50 mL of acetonitrile is added 0.92 g (0.0048 mol) of methyl-p-toluenesulfonate at 0°C under a nitrogen atmosphere. The reaction mixture is heated at 80°C for 20 hours and the resulting polymer solution is then refluxed with 2.3 mL distilled water in the presence of 5.6 g (0.0528 mol) of sodium carbonate for 24 hours. The solvents are removed under vacuum. The residue is

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extracted with 300 mL of dichloromethane for 24 hours, and the insolubles are removed by suction filtration. The dichloromethane is then evaporated to yield about 48 g (96% yield) of poly(2-ethyl-2-oxazoline) alcohol.

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EXAMPLE IISynthesis of Acrylate-Capped Poly(2-ethyl-2-oxazoline) Alcohol Macromonomer

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To a solution of 48 g of poly(2-ethyl-2-oxazoline) alcohol (from EXAMPLE I) and 1.0 g (0.01056 mol) of triethylamine in 80 mL of dichloromethane is added dropwise a solution of 0.95 g (0.01056 mol) of acryloyl chloride at 0°C under a nitrogen atmosphere. The reaction mixture is then stirred at room temperature for 36 hrs, and the resulting solution is then suction filtered to remove the insolubles. The solvent and any unreacted triethylamine are removed by evaporation under vacuum. The resulting solid is then redissolved in 200 mL of dichloromethane, filtered, and evaporated under vacuum to yield about 45.6 g (95% yield) of the macromonomer.

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Using an analogous procedure the methacrylate and ethacrylate endcapped macromonomers are prepared by replacing the acryloyl chloride with an equivalent molar amount of methacryloyl chloride and ethacryloyl chloride, respectively.

EXAMPLE III

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Synthesis of Vinylbenzyl-Capped Poly(2-ethyl-2-oxazoline) Alcohol Macromonomer

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To a solution of 50 g (0.5044 mol) of 2-ethyl-2-oxazoline in 50 mL of acetonitrile is added a mixture of 0.3816 g (0.0025 mol) of meta and paravinylbenzylchlorides (available from Aldrich Chemical Co.), 0.562 g (0.0037 mol) of sodium iodide and 0.06 g (0.00023 mol) of N,N'-diphenyl-p-phenylenediamine. The solution is then heated at 90°C for 16 hours. To the resulting reaction product is added 100 mL of dichloromethane and the solution is filtered and then precipitated in 800 mL of ether. The precipitate product is collected by vacuum filtration and dried

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under vacuum at ambient temperature to yield about 45 g (90% yield) of the macromonomer.

EXAMPLE IV

5 Synthesis of Acrylate-Capped Poly(ethylene glycol)methyl Ether Macromonomer

10 To a solution of 50 g (0.01 mol) of poly(ethylene glycol)methyl ether having an average molecular weight of about 5000 (commercially available from Aldrich Chemical Co.) and 4.05 g (0.04 mol) of triethylamine in 400 mL of dichloromethane is added dropwise at 0°C under a nitrogen atmosphere a solution of 2.26 g (0.025 mol) of acryloyl chloride dissolved in 25 mL of dichloromethane. The reaction mixture is then stirred at room temperature for 36 hrs, and the resulting solution is then suction
15 filtered to remove the insolubles. The solvent and any unreacted triethylamine are removed by evaporation under vacuum. The resulting solid is then redissolved in 300 mL of dichloromethane, filtered, and evaporated under vacuum to yield about 50 g (100% yield) of the macromonomer.

20 The above procedure is varied using other poly(ethylene glycol)alkyl ethers (e.g. methyl, ethyl, 2-ethylhexyl, decyl, dodecyl, cetyl, stearyl, lauryl, and myristyl wherein the polymer has an average molecular weight varying from about 1000 to about 200,000) to obtain the analogous acrylate-capped macromonomers.
25 Additionally, the methacrylate and ethacrylate endcapped macromonomers are prepared by replacing the acryloyl chloride with an equivalent molar amount of methacryloyl chloride and ethacryloyl chloride, respectively.

30 EXAMPLE V

Synthesis of Poly(n-butyl acrylate)-graft-poly(2-ethyl-2-oxazoline) Thermoplastic Elastomeric Copolymer

35 To a solution of 16.0 g (0.1248 mol) of n-butyl acrylate, and 4 g of acrylate capped poly(2-ethyl-2-oxazoline) macromonomer

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(from Example II) in 100 mL of acetone is added 0.03 g (0.00018 mol) of azoisobutyronitrile (AIBN) initiator. The resulting solution is refluxed slowly for about 20 hours. The reaction is then quenched by the addition of about 5 mL of methanol. The solution is then poured into a teflon pan and the acetone is evaporated at room temperature under a fume hood. The resulting polymer film is redissolved in ethanol, filtered, and the ethanol is then evaporated to yield about 18.4 g of the thermoplastic elastomeric copolymer.

Alternatively, by varying the monomers and macromonomers used, this procedure is used to prepare other copolymers of the present invention.

EXAMPLE VI

Synthesis of Poly(n-butyl-co-2-methoxyethylacrylate)-graft-poly(2-ethyl-2-oxazoline) Thermoplastic Elastomeric Copolymer: Method I

To a solution of 4.5 g (0.035 mol) of *n*-butyl acrylate, 2.5 g (0.0192 mol) of 2-methoxy ethylacrylate and 3 g poly(2-ethyl-2-oxazoline) macromonomer (from Example II) in 40 mL of acetone is added 0.05 g of AIBN initiator. The resulting solution is refluxed slowly for about 20 hours. The reaction is then quenched by the addition of about 5 mL of methanol. The solution is then poured into a teflon pan and the acetone is evaporated at room temperature under a fume hood. The resulting polymer film is redissolved in ethanol, filtered, and the ethanol is then evaporated to yield about 9.5 g of the thermoplastic elastomeric copolymer.

Alternatively, by varying the monomers and macromonomers used, this procedure is used to prepare other copolymers of the present invention.

EXAMPLE VII

Synthesis of Poly(n-butyl-co-2-methoxyethylacrylate)-graft-poly(2-ethyl-2-oxazoline) Thermoplastic Elastomeric Copolymer: Method II

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To a 500 mL round-bottomed flask is added 20.8 g (0.1623 mol) of *n*-butyl acrylate, 11.2 g (0.0861 mol) of 2-methoxyethyl acrylate, 0.30 g (0.002 mol) *p*-vinylbenzyl chloride, and 0.02 g (0.0012 mol) of azoisobutyronitrile (AIBN) initiator, in 200 mL of acetone. The resulting solution is refluxed slowly for about 24 hours. The reaction is then quenched by the addition of about 5 mL of methanol and cooled to room temperature. The solvents are removed by rotary evaporation and the resulting polymer is dissolved in 250 mL of dry acetonitrile. Next 20.0 g (0.2018 mol) of 2-ethyl-2-oxazoline and 0.44 g (0.0029 mol) of sodium iodide is added and the solution is heated to 90°C for 20 hours. The resulting solution is filtered and the solvent is evaporated to yield about 45.0 g (86% yield) of the thermoplastic elastomeric copolymer.

Alternatively, by varying the monomers used, this procedure is used to prepare other copolymers of the present invention.

EXAMPLE VIII

Synthesis of Poly(*n*-butyl-co-2-(dimethylamino)ethyl methacrylate)-graft-poly(2-ethyl-2-oxazoline) Thermoplastic Elastomeric

To a solution of 7.2 g (0.0561 mol) of *n*-butyl acrylate, 4.8 g (0.0305 mol) of 2-(dimethylamino)ethyl methacrylate, and 8.0 g poly(2-ethyl-2-oxazoline) macromonomer (from Example II) in 80 mL of acetone is added 0.01 g of AIBN initiator. The resulting solution is refluxed slowly for about 24 hours. The reaction is then quenched by the addition of about 5 mL of methanol. The solution is then poured into a teflon pan and the acetone is evaporated at room temperature under a fume hood. The resulting polymer film is redissolved in ethanol, filtered, and the ethanol is then evaporated to yield about 18.4 g of the thermoplastic elastomeric copolymer.

Alternatively, by varying the monomers and macromonomers used, this procedure is used to prepare other copolymers of the present invention.

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EXAMPLE IXSynthesis of Methyl Quaternized Poly(n-butyl-co-2-(dimethylamino)-ethyl methacrylate)graft-poly(2-ethyl-2-oxazoline) Thermoplastic Elastomeric Copolymer

5 To 10 grams of the copolymer from EXAMPLE VIII dissolved in 80 grmas of ethanol is added dropwise 4.32 g (0.0281 mole) of dimethylsulfate. The resulting solution is stirred for 2 hours at room temperature. The solvent is removed by rotary evorpatation to yield about 10 grams of the methyl quaternized copolymer.

10

EXAMPLE XHair Spray

Hair spray compositions are prepared from the following components utilizing conventional mixing techniques.

15

	<u>Ingredients</u>				<u>Weight %</u>			
	A	B	C	D	A	B	C	D
Water	QS 100	QS 100	QS 100	QS 100				
Ethanol (SDA 40)	79.0	79.0	79.0	90.0				
Copolymer of Example VI ¹	4.0	4.0	3.0	3.0				
20 Fragrance	0.1	0.2	---	---				

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These products are prepared by first dissolving the polymer in the ethanol with stirring. The water and fragrance are then added with stirring. The resulting hair spray compositions can then be packaged in a nonaerosol spray pump. Alternatively, the compositions can be combined with conventional propellants and packaged in an aerosol spray.

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These hair sprays are useful for application to the hair to provide a styling and holding benefit.

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¹ Alternatively, spray compositions are prepared using the copolymers of Examples V and VIII.

35

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EXAMPLE XIReduced Volatile Organic Content Hairspray

Hair spray compositions are prepared from the following components utilizing conventional mixing techniques.

5	<u>Ingredients</u>	<u>Weight %</u>			
		<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
	Water	QS 100	QS 100	QS 100	QS 100
	Ethanol (SDA 40)	54.0	54.0	54.0	54.0
	Copolymer of Example VII ¹	4.0	3.0	4.0	3.0
10	Fragrance	0.05	0.2	---	---

These products are prepared by first dissolving the polymer in the ethanol with stirring. The water and fragrance are then added with stirring. The resulting hair spray compositions can then be packaged in a nonaerosol spray pump. Alternatively, the compositions can be combined with conventional propellants and packaged in an aerosol spray.

These hair sprays are useful for application to the hair to provide a styling and holding benefit.

¹ Alternatively, spray compositions are prepared using the copolymers of Examples V and VIII.

EXAMPLE XII25 Mousse

Mousse compositions are prepared from the following components utilizing conventional mixing techniques.

30	<u>Ingredients</u>	<u>Weight %</u>		
		<u>A</u>	<u>B</u>	<u>C</u>
	Water	QS 100	QS 100	QS 100
	Copolymer of Example VIII ¹	3.00	2.50	3.50
	Lauramide DEA	0.33	0.33	0.33
	Sodium Methyl Oleyl Taurate	1.67	1.67	1.67
	DMDM Hydantoin	0.78	0.78	0.78
35	Disodium EDTA	0.20	0.20	0.20

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Polyoxyalkylated isostearyl

Alcohol ²	0.10	0.10	0.10
Fragrance	0.10	0.10	0.10
Propellant ³	7.0	7.0	7.0

5

These products are prepared by first dissolving the polymer in water with stirring. The remaining ingredients, except the propellant, are then added with stirring.

10

The resulting mousse concentrate can then be combined with conventional propellants (e.g., Propellant A46) and packaged in an aerosol spray.

These mousses are useful for application to the hair to provide a styling and holding benefit.

15

¹ Alternatively, mousse compositions are prepared using the copolymers of Examples V and VI.

² Available as Aerosurf 66-E10.

³ Available as a mixture of 82.46% isobutane, 16.57% propane, and 0.001% butane.

20

EXAMPLE XIIIHair Tonic

25

Hair tonic compositions are prepared from the following components utilizing conventional mixing techniques.

IngredientsWeight %

	A	B	C
Ethanol (SDA 40)	QS 100	QS 100	QS 100
Copolymer of Example VI ¹	0.75	1.00	1.25
30 Fragrance	0.10	0.20	0.30

35

These products are prepared by dissolving the polymer in the ethanol with stirring and then adding the fragrance and any colors.

-50-

These hair tonics are useful for application to the hair to provide a styling and holding benefit.

- 5 1 Alternatively, tonic compositions are prepared using the copolymers of Examples V and VIII.

EXAMPLE XIV

Hair Conditioner

- 10 A hair conditioner composition is prepared from the following components utilizing conventional mixing techniques.

<u>Ingredient</u>	<u>Weight %</u>
<u>Styling Agent Premix</u>	
Copolymer of Example IX	1.00
<u>Silicone Premix</u>	
Silicone gum, GE SE76 ¹	0.30
Octamethyl cyclotetrasiloxane	1.70
<u>Main Mix</u>	
20 Water	QS100
Cetyl Alcohol	1.00
Quaternium 18 ²	0.85
Stearyl Alcohol	0.70
Hydroxethyl cellulose	0.50
25 Cetareth-20	0.35
Fragrance	0.20
Dimethicone copolyol	0.20
Citric Acid	0.13
Methylchloroisothiazolinone (and)	
30 methylisothiazolinone	0.04
Sodium Chloride	0.01

- 35 The product is prepared by comixing all the Main Mix ingredients, heating to about 60°C with mixing, and colloid milling while cooling to about 45°C. At this temperature, the two

-51-

premixes are added separately with moderate agitation and the resultant conditioner is allowed to cool to room temperature.

This product is useful as a rinse off hair conditioner.

- 5 1 Commercially available from General Electric.
 2 Dimethyl Di(Hydrogenated Tallow) Ammonium Chloride

EXAMPLE XV

Shampoo Composition

- 10 A shampoo composition is prepared from the following components utilizing conventional mixing techniques.

	<u>Ingredients</u>	<u>Weight %</u>
	<u>Styling Agent</u>	
15	Copolymer from Example IX	1.00
	<u>Premix</u>	
	Silicone gum	0.50
20	Dimethicone, 350 cs fluid	0.50
	<u>Main Mix</u>	
	Water	QS100
	Ammonium lauryl sulfate	11.00
	Cocamide MEA	2.00
25	Ethylene glycol distearate	1.00
	Xanthan Gum	1.20
	Methylchloroisothiazolinone (and)	
	methylisothiazolinone	0.04
30	Citric Acid to pH 4.5 as needed	

- 35 The Main Mix is prepared by first dissolving the xanthan gum in the water with conventional mixing. The remaining Main Mix ingredients are added and the Main Mix is heated to 150°F with agitation for 1/2 hour. The Styling Agent and the Premix are then added sequentially with about 10 minutes of agitation between

-52-

additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particle size, the Styling Agent and Premix can be added at different times using either or both high shear mixing (high speed dispersator) or normal agitation.

This shampoo is useful for cleansing the hair and for providing a styling benefit.

Example XVI

Anti-Acne Composition

An anti-acne composition is made by combining the following components using conventional mixing technology.

<u>Ingredient</u>	<u>Weight %</u>
Water	QS100
Salicylic Acid	2.0
Copolymer from Example VI ¹	2.0
Ethanol (SDA 40)	40.0

The composition displays skin penetration of the salicylic acid as well as improved skin feel and residue characteristics and is useful for the treatment of acne.

¹ Alternatively, the anti-acne compositions are prepared using the copolymers of Examples VIII and IX.

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Example XVIITopical Analgesic Composition

A topical analgesic composition is made by combining the following ingredients utilizing conventional mixing techniques.

5	<u>Ingredient</u>	<u>Weight %</u>
	Water, Purified	QS100
	Ibuprofen	2.0
	Copolymer from Example VI ¹	2.0
10	Ethanol (SDA 40)	20.0

The compositions display skin penetration of the ibuprofen active as well as improved skin feel and residue characteristics together with excellent moisturizing, emolliency, rub-in and absorption characteristics.

¹ Alternatively, the topical analgesic compositions are prepared using the copolymers of Examples VIII and IX.

Example XVIIISunless Tanning Composition

A composition for sunless tanning is made by combining the following ingredients utilizing conventional mixing techniques.

25	<u>Ingredients</u>	<u>Weight %</u>
	<u>Phase A</u>	
	Water	qs 100
	Copolymer from Example VI ¹	2.00
	Carbomer 934 ²	0.20
30	Carbomer 980 ³	0.15
	Acrylic Acid Copolymer ⁴	0.15
	<u>Phase B</u>	
35	PPG-20 Methyl Glucose Ether	
	Distearate	2.00

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	Tocopheryl Acetate	1.20
	Mineral Oil	2.00
	Stearyl Alcohol	1.00
	Shea Butter	1.00
5	Cetyl Alcohol	1.00
	Ceteareth-20	2.50
	Ceteth-2	1.00
	Ceteth-10	1.00
10	<u>Phase C</u>	
	DEA-Cetyl Phosphate	0.75
	<u>Phase D</u>	
15	Dihydroxyacetone	3.00
	<u>Phase E</u>	
	Butylene Glycol	2.00
	DMDM Hydantoin (and)	
20	Iodopropynyl Butylcarbamate	0.25
	<u>Phase F</u>	
	Fragrance	1.00
	Cyclomethicone	2.00

25 In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85°C. In a separate vessel the Phase B ingredients are combined and heated to 85-90°C until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture is then added to Phase A to

30 form the emulsion. The emulsion is cooled to 40-45°C with continued mixing. Next, in a separate vessel, the dihydroxyacetone is dissolved in water and the resulting solution is mixed into the emulsion. In another vessel, the Phase E ingredients are heated with mixing to 40-45°C until a clear

35 solution is formed and this solution is then added to the

-55-

emulsion. Finally, the Phase F ingredients are added to the emulsion with mixing, which is then cooled to 30-35°C, and then to room temperature.

5 This emulsion is useful for topical application to the skin to provide an artificial tan.

1 Alternatively, the artificial tanning compositions are prepared using the copolymers of Examples VIII and IX.

2 Available as Carbopol^R 934 from B.F. Goodrich.

10 3 Available as Carbopol^R 980 from B.F. Goodrich.

4 Available as Pemulen TR1 from B.F. Goodrich.

EXAMPLE XIX

15 Sunscreen Composition

An oil-in-water emulsion is prepared by combining the following components utilizing conventional mixing techniques.

	<u>Ingredients</u>	<u>Weight %</u>
20	<u>Phase A</u>	
	Water	QS100
	Carbomer 954 ¹	0.24
	Carbomer 1342 ²	0.16
	Copolymer from Exmaple VII ³	1.75
25	Disodium EDTA	0.05
	<u>Phase B</u>	
	Isoarachidyl Neopentanoate ⁴	2.00
	PVP Eicosene Copolymer ⁵	2.00
30	Octyl Methoxycinnamate	7.50
	Octocrylene	4.00
	Oxybenzone	1.00
	Titanium Dioxide	2.00
	Cetyl Palmitate	0.75
35	Stearoxytrimethylsilane	

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	(and) Stearyl Alcohol ⁶	0.50
	Glyceryl Tribehenate ⁷	0.75
	Dimethicone	1.00
5	Tocopheryl Acetate	0.10
	DEA-Cetyl Phosphate	0.20

Phase C

	Water	2.00
10	Triethanolamine 99%	0.60

Phase D

	Water	2.00
	Butylene Glycol	2.00
15	DMDM Hydantoin (and)	
	Iodopropynyl Butylcarbamate ⁸	0.25
	dL Panthenol	1.00

Phase E

20	Cyclomethicone	1.00
----	----------------	------

1 Available as Carbopol^R 954 from B.F. Goodrich.

2 Available as Carbopol^R 1342 from B.F. Goodrich.

3 Alternatively, the sunscreen compositions are prepared using the copolymers of Examples VIII and IX.

25 4 Available as Elefac I-205 from Bernel Chemical.

5 Available as Ganex V-220 from GAF Corporation.

6 Available as DC 580 Wax from Dow Corning.

7 Available as Synchronowax HRC from Croda.

30 8 Available as Glydant Plus from Lonza.

35 In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85°C. In a separate vessel the Phase B ingredients (except DEA-Cetyl Phosphate) are combined and heated to 85-90°C until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture

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is then added to Phase A to form the emulsion. The Phase C ingredients are combined until dissolved and then added to the emulsion. The emulsion is then cooled to 40-45°C with continued mixing. In another vessel, the Phase D ingredients are heated with mixing to 40-45°C until a clear solution is formed and this solution is then added to the emulsion. Finally, the emulsion is cooled to 35°C and the Phase E ingredient is added and mixed.

This emulsion is useful for topical application to the skin to provide protection from the harmful effects of ultraviolet radiation.

EXAMPLE XX

Facial Moisturizer

A leave-on facial emulsion composition containing a cationic hydrophobic surfactant is prepared by combining the following components utilizing conventional mixing techniques.

	<u>Ingredient</u>	<u>Weight %</u>
20	Water	QS100
	Copolymer from Example VI ¹	1.00
	Glycerin	3.00
	Cetyl Palmitate	3.00
	Cetyl Alcohol	1.26
	Quaternium-22	1.00
25	Glyceryl Monohydroxy Stearate	0.74
	Dimethicone	0.60
	Stearic Acid	0.55
	Octyldodecyl Myristate	0.30
	Potassium Hydroxide	0.20
30	Carbomer 1342	0.125
	Tetrasodium EDTA	0.10
	DMDM Hydantoin and Iodopropynyl	
	Butyl Carbamate	0.10
35	Carbomer 951	0.075

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This emulsion is useful for application to the skin as a moisturizer.

1 Alternatively, the moisturizers are prepared using the
5 copolymers of Examples VIII and IX.

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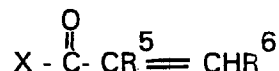
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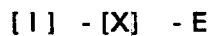
What is Claimed is:

1. A water or alcohol soluble or dispersible thermoplastic elastomeric copolymer having a backbone and two or more polymeric side chains, said copolymer formed from the copolymerization of randomly repeating A and B units wherein said copolymer comprises:
 - (i) from 40% to 90% by weight of said A units, wherein said A units are polymerizable monomer units; and
 - (ii) from 10% to 60% by weight of said B units, wherein said B units are hydrophilic macromonomer units, copolymerizable with A, whereby said macromonomer units form said polymeric side chains; andwherein said copolymer has a weight average molecular weight greater than 10,000, and wherein said copolymer exhibits two distinct T_g values, said first T_g corresponding to said backbone and having a value less than 0°C, and said second T_g corresponding to said polymeric side chains and having a value greater than 25°C.
2. A copolymer according to Claim 1 wherein the T_g corresponding to said backbone is from -55°C to -120°C, and the T_g corresponding to said polymeric side chains is from 35°C to 150°C.
3. A copolymer according to Claim 2 wherein said A monomer units comprise from 50% to 85% by weight of the total copolymer and said B macromonomer units comprise from 15% to 50% by weight of the total copolymer, preferably wherein said A monomer units comprise from 60% to 80% by weight of the total copolymer and said B macromonomer units comprise from 20% to 40% by weight of the total copolymer and said A monomer units are ethylenically unsaturated monomer units and said copolymer has a weight average molecular weight from 10,000 to 5,000,000.

4. A copolymer according to Claim 3 wherein said A monomer units are of the formula



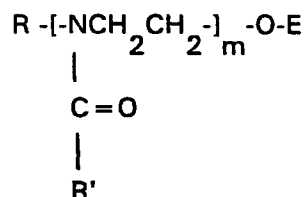
wherein X is selected from the group consisting of -OH, -OM, -OR⁴, -NH₂, -NHR⁴, and -N(R⁴)₂; M is a cation selected from the group consisting of Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺, Zn⁺⁺, NH₄⁺, alkylammonium, dialkylammonium, trialkylammonium, and tetralkylammonium; R⁴ is selected from the group consisting of H, C₁₋₈-straight or branched chain alkyl, N,N-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl; and R⁵ and R⁶ are independently selected from the group consisting of H, C₁₋₈-straight or branched chain alkyl, methoxy, ethoxy, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl, preferably wherein said A monomer units are selected from the group consisting of n-butyl acrylate, 2-ethylhexyl acrylate, N-octyl acrylamide, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate, N,N-dimethylaminoethyl acrylate, and mixtures thereof; and wherein said B macromonomer units are of the formula:



wherein X is a hydrophilic monomer unit selected from the group consisting of oxazolines, N-alkyloxazolines, alkylene glycols, N-vinylpyrrolidones, N-allylpyrrolidones, vinylpyridines, allylpyridines, vinylcaprolactams, allylcaprolactams, vinylimidazoles, allylimidazoles, vinylfurans, allylfurans, vinyltetrahydrofurans, allyltetrahydrofurans, and mixtures thereof; m is an integer from 10 to 2000; E is an ethylenically unsaturated endcapping moiety, copolymerizable with A, selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, and mixtures thereof; I is a

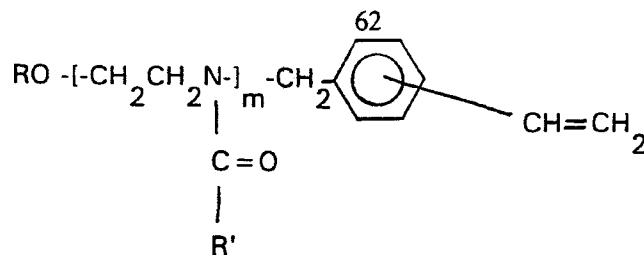
chemical moiety derived from an initiator selected from the group consisting of cationic initiators, anionic initiators, and free radical initiators; and n is an integer selected from 0 and 1, preferably wherein said chemical moiety I is selected from the group consisting of H, hydroxy, methyl, ethyl, methoxy, ethoxy, and mixtures thereof.

5. A copolymer according to Claim 4 wherein said B macromonomer units are selected from the group consisting of endcapped poly(N-alkyloxazolines), endcapped polyalkylene glycol monoalkyl ethers, and mixtures thereof.
6. A copolymer according to Claim 5 wherein said endcapped poly(N-alkyloxazoline) macromonomers are of the formula



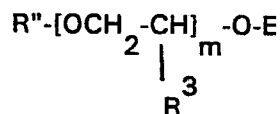
wherein R and R' are independently selected from the group consisting of H and C₁₋₈ straight or branched chain alkyl; m is an integer from 10 to 2000; and E is an ethylenically unsaturated moiety, copolymerizable with A, selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzoyl, 4-vinylbenzoyl, and mixtures thereof, preferably wherein R is methyl and R' is ethyl, and m is an integer from 20 to 250.

7. A copolymer according to Claim 5 (wherein said endcapped poly(N-alkyloxazoline) macromonomers are of the formula



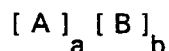
wherein R and R' are independently selected from the group consisting of H and C₁₋₈ straight or branched chain alkyl; and m is an integer from 10 to 2000, preferably wherein R is selected from the group consisting of H and methyl, and R' is ethyl, and m is an integer from 20 to 250.

8. A copolymer according to Claim 5 wherein said endcapped polyalkylene glycol monoalkyl ether macromonomers are of the formula



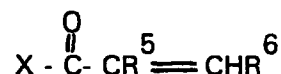
wherein R'' is selected from the group consisting of C₁₋₄₀ straight or branched chain alkyl; R³ is selected from the group consisting of H, and C₁₋₈ straight or branched chain alkyl; m is an integer from 20 to 2000; and E is an ethylenically unsaturated moiety copolymerizable with A, selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzoyl, 4-vinylbenzoyl and mixtures thereof, preferably wherein R'' is methyl and R³ is H, and m is an integer from 40 to 500.

9. A water or alcohol soluble or dispersible thermoplastic elastomeric copolymer having a backbone and one or more polymeric side chains, said copolymer formed from the copolymerization of randomly repeating A and B units and corresponding to the formula



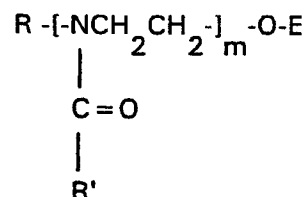
wherein

- (i) A is at least one polymerizable monomer unit corresponding to the formula



wherein X is selected from the group consisting of $-OH$, $-OM$, $-OR^4$, $-NH_2$, $-NHR^4$, and $-N(R^4)_2$; M is a cation selected from the group consisting of Na^+ , K^+ , Mg^{++} , Ca^{++} , Zn^{++} , NH_4^+ , alkylammonium, dialkylammonium, trialkylammonium, and tetraalkylammonium; each R^4 is selected from the group consisting of H , C_{1-8} straight or branched chain alkyl, N,N -dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl; and R^5 and R^6 are independently selected from the group consisting of H , C_{1-8} straight or branched chain alkyl, methoxy, ethoxy, 2-hydroxyethoxy, 2-methoxyethyl, and 2-ethoxyethyl, preferably wherein said A monomer units are selected from the group consisting of n -butyl acrylate, 2-ethylhexyl acrylate, N -octyl acrylamide, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate, N,N -dimethylaminoethyl acrylate, and mixtures thereof; R is methyl, R' is ethyl, m is an integer from 10 to 2000, a is an integer from 100 to 3000, and b is an integer from 2 to 50;

(ii) B is at least one hydrophilic macromonomer unit copolymerizable with A corresponding to the formula

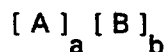


wherein E is an ethylenically unsaturated moiety, copolymerizable with A, selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzoyl, and 4-vinylbenzoyl; R and R' are independently selected from the group consisting of H and C₁-C₈ straight or branched chain alkyl; and m is an integer from 10 to 2000; and

(iii) a is an integer of 100 or greater and b is an integer of 2 or greater; and

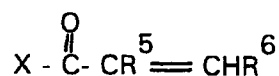
wherein said copolymer exhibits two distinct T_g values, said first T_g corresponding to said backbone and having a value less than 0°C, and said second T_g corresponding to said polymeric side chains and having a value greater than 25°C.

10. A water or alcohol soluble or dispersible thermoplastic elastomeric copolymer having a backbone and one or more polymeric side chains, said copolymer formed from the copolymerization of randomly repeating A and B units and corresponding to the formula



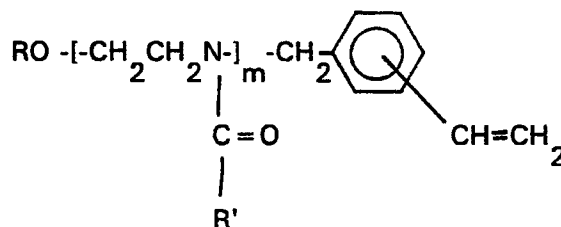
wherein

- (i) A is at least one polymerizable monomer unit corresponding to the formula



wherein X is selected from the group consisting of $-OH$, $-OM$, $-OR$, $-NH$, $-NHR$, and $-N(R)$; M is a cation selected from the group consisting of Na^+ , K^+ , Mg^{++} , Ca^{++} , Zn^{++} , NH_4^+ , alkylammonium, dialkylammonium, trialkylammonium, and tetraalkylammonium; each R is selected from the group consisting of H , C_1 - C_8 straight or branched chain alkyl, and N,N -dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, 2-ethoxyethyl; and R^5 and R^6 are independently selected from the group consisting of H , C_1 - C_8 straight or branched chain alkyl, methoxy, ethoxy, and 2-hydroxyethoxy, 2-methoxyethyl, 2-ethoxyethyl, preferably wherein said A monomer units are selected from the group consisting of n -butyl acrylate, 2-ethylhexyl acrylate, N -octyl acrylamide, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate, N,N -dimethylaminoethyl acrylate, and mixtures thereof; R is selected from the group consisting of H and methyl, R' is ethyl, m is an integer from 10 to 2000, a is an integer from 100 to 3000, and b is an integer from 2 to 50;

- (ii) B is at least one hydrophilic macromonomer unit copolymerizable with A corresponding to the formula

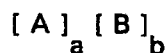


wherein R and R' are independently selected from the group consisting of H and C₁₋₈ straight or branched chain alkyl; and m is an integer from 10 to 2000; and

(iii) a is an integer of 100 or greater and b is an integer of 2 or greater; and

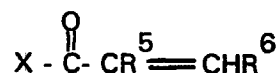
wherein said copolymer has a weight average molecular weight greater than 10,000, and wherein said copolymer exhibits two distinct T_g values, said first T_g corresponding to said backbone and having a value less than 0°C, and said second T_g corresponding to said side chains and having a value greater than 25°C.

11. A water or alcohol soluble or dispersible thermoplastic elastomeric copolymer having a backbone and one or more polymeric side chains, said copolymer formed from the copolymerization of randomly repeating A and B units and corresponding to the formula



wherein

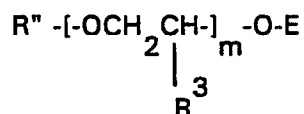
- (i) A is at least one polymerizable monomer unit corresponding to the formula



wherein X is selected from the group consisting of -OH, -OM, -OR, -NH₂, -NHR, and -N(R)₂; M is a cation selected from the group consisting of Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺, Zn⁺⁺, NH₄⁺, alkylammonium, dialkylammonium, trialkylammonium, and tetralkylammonium; each R is independently selected

from the group consisting of H, C₁-C₈ straight or branched chain alkyl, and N,N-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, 2-ethoxyethyl; and R⁵ and R⁶ are independently selected from the group consisting of H, C₁-C₈ straight or branched chain alkyl, methoxy, ethoxy, and 2-hydroxyethoxy, 2-methoxyethyl, 2-ethoxyethyl, preferably wherein said A monomer units are selected from the group consisting of n-butyl acrylate, 2-ethylhexyl acrylate, N-octyl acrylamide, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate, N,N-dimethylaminoethyl acrylate, and mixtures thereof; R⁷ is methyl, R³ is H, m is an integer from 20 to 2000, a is an integer from 100 to 3000, and b is an integer from 2 to 50;

(ii) B is at least one hydrophilic macromonomer unit copolymerizable with A corresponding to the formula



wherein E is an ethylenically unsaturated moiety, copolymerizable with A, selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzoyl, 4-vinylbenzoyl, and mixtures thereof; R⁷ is selected from the group consisting of C₁-C₄₀ straight or branched chain alkyl; R³ is selected from the group consisting of H, and C₁-C₈ straight or branched chain alkyl; and m is an integer from 20 to 2000; and

(iii) a is an integer of 100 or greater and b is an integer of 2 or greater; and

wherein said copolymer has a weight average molecular weight greater than 10,000, and wherein said copolymer exhibits two distinct T_g values, said first T_g corresponding to said backbone and having a value less than 0°C, and said second

T_g corresponding to said polymeric side chains and having a value greater than 25°C.

12. A hair care composition useful for styling hair, comprising the copolymer of Claim 1 and a carrier suitable for application to the hair.
13. A hair care composition according to Claim 12, in the form of a liquid suitable for application to the hair, wherein said carrier comprises water, a C1-C6 monohydric alcohol, or a mixture thereof, preferably which further comprises a propellant.
14. A hair care composition according to Claim 12, in the form of a mousse for application to the hair, wherein said carrier comprises water, one or more surfactants, and a propellant.
15. A composition for topical application to the skin comprising the copolymer of Claim 1 and a carrier suitable for application to the skin.
16. A skin care composition useful for delivering pharmaceutical actives to the skin, comprising the copolymer of Claim 1, a pharmaceutically active agent, and a pharmaceutically acceptable carrier, preferably wherein said pharmaceutically active agent is selected from the group consisting of anti-acne drugs, non-steroidal anti-inflammatory drugs, antipruritic drugs, anesthetic drugs, antimicrobial drugs, sunscreening agents, sunless tanning agents, skin bleaching agents, and mixtures thereof.
17. A hair care composition useful for styling hair, comprising the copolymer of any of Claims 9, 10, or 11 and a carrier suitable for application to the hair.

18. A composition for topical application to the skin comprising the copolymer of any of Claims 9, 10, or 11 and a carrier suitable for application to the skin.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/07387

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C08F290/06 A61K7/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C08F A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US,A,4 910 268 (KOBAYASHI) 20 March 1990 see column 1, line 12 - line 22; example 31 ---	1-7,9,10 1-18
X	DATABASE WPI Section Ch, Week 9112, Derwent Publications Ltd., London, GB; Class A14, AN 91-083213 'Dispersing agent' & JP,A,3 028 202 (NIPPON SHOKUBAI K.) 6 February 1991 see abstract	1-5,8,11
Y	---	1-18
X	WO,A,91 15186 (PROCTER & GAMBLE) 17 October 1991 see claims; example IV --- -/--	1-3

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/07387

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MAKROMOL. CHEM., vol.187, no.8, 13 August 1986 pages 1895 - 1906 ATSUSHI MARUYAMA ET AL. 'Synthesis and characterization of polyamine graft copolymers ...' ---	1-3
X	MAKROMOL. CHEM., vol.188, no.6, 26 June 1986 pages 1347 - 1354 S. SOSNOWSKI ET AL. 'anionic living polymerization ...' ----	1-3
X	US,A,5 153 273 (KOBAYASHI) 6 October 1992 see column 1, line 13 - line 17; examples 12-13 -----	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/07387

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4910268	20-03-90	JP-A- 2000603	05-01-90
WO-A-9115186	17-10-91	US-A- 5120531	09-06-92
		AU-A- 7674291	30-10-91
		CN-A- 1056053	13-11-91
US-A-5153273	06-10-92	JP-A- 2281034	16-11-90

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Published:

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 00/71606 A1

(54) Title: POLYSILOXANE BLOCK COPOLYMERS IN TOPICAL COSMETIC AND PERSONAL CARE COMPOSITIONS

(57) Abstract: A process for making a polysiloxane block copolymer which is built up from units of the formula [A] [B], in which A is a polymeric block built up from radically polymerisable monomer, and B is a polysiloxane block, the process comprising the steps of forming a polysiloxane macroinitiator by grafting a radical initiator onto a polysiloxane via a nucleophilic displacement reaction between groups on the polysiloxane and radical initiator respectively, and reacting the polysiloxane macroinitiator so obtained with radically polymerisable monomers in an atom transfer radical polymerisation reaction to form a polysiloxane block copolymer. Also provided are cosmetic and personal care compositions, such as hair styling compositions, containing the polysiloxane block copolymers.

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**POLYSILOXANE BLOCK COPOLYMERS IN TOPICAL COSMETIC AND
PERSONAL CARE COMPOSITIONS**

5 Field of the Invention

The present invention relates to polysiloxane block copolymers suitable for use in cosmetic and personal care compositions, their preparation, and to cosmetic and
10 personal care compositions, such as hair styling compositions, containing the polysiloxane block copolymers.

Background and Prior Art

15 Cosmetic and personal care compositions such as hair styling sprays, mousses, gels and shampoos, frequently contain resins, gums and adhesive polymers to provide a variety of benefits, for example, film-forming ability, thickening, sensory properties and hair shaping and setting.

20 Polymers for use in such compositions include organic or silicone-containing linear or graft copolymers which contain various monomers in an alternating, random, block or homopolymer configuration.

25 Graft copolymers are known for use as film-forming polymers in hair care and other personal care compositions. These graft copolymers typically comprise a polymeric backbone and one or more macromonomers grafted to the backbone, in which
30 the physical and chemical attributes such as glass transition temperature and water solubility can be selected

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independently for the polymeric backbone and macromonomer grafts in order to provide the desired overall polymer properties.

- 5 For example, WO95/01383 and WO95/01384 describe the use of water or alcohol soluble or dispersible graft copolymers in hair and skin care compositions, in which the copolymer has a backbone and two or more polymeric side chains, and is formed by copolymerisation of randomly repeating monomer
- 10 units A and B. Monomer A is selected to have a hydrophobic character and macromonomer B comprises a long hydrophilic part. EP 412,704, EP 408,313 and EP 412,707 have suggested the use of silicone grafted acrylate copolymers in hair care applications. US 4,988,506 describes the use of non-pressure
- 15 sensitive polysiloxane-grafted copolymers in hair care compositions.

Block copolymers have an advantage over graft copolymers in that the polymer architecture can be controlled more

20 closely. This is particularly important when designing polymers with segments of distinct physical and chemical properties for particular applications, e.g. alternating "hard" and "soft" segments in a hairspray polymer for improved hold and feel.

- 25 US 5,468,477 describes cosmetics and personal care compositions containing a vinyl-silicone graft or block copolymer comprising a silicone polymer segment and a vinyl polymer segment. This block or graft copolymer is prepared
- 30 by the radical polymerisation of a mercapto functional silicone chain transfer agent and vinyl monomers. Copolymers

- 3 -

prepared by this method generally have a low molecular weight and a low silicone content due to premature chain termination. Also, intramolecular cross-linking reactions lead to polymer build up in an uncontrolled manner, and
5 hence polydisperse systems with a mixture of chain lengths and molecular architectures. Furthermore, the presence of mercapto groups is a disadvantage in personal care applications since they tend to decompose to give odour problems.

10

Another approach to the synthesis of block copolymers is to use organopolysiloxane macroinitiators, which are organopolysiloxanes which contain groups which form radicals. These are described in US 5,523,365 and used in
15 WO98/48771, where a polydimethylsiloxane macroinitiator with azo groups is used to synthesise a block copolymer. Problems include the expense and safety hazards associated with the radical macroinitiator, which has to be present in significant quantities, otherwise there will be insufficient siloxane
20 content in the final product. Furthermore, the size of the polydimethylsiloxane macroinitiator means that the reaction is inefficient, and large quantities of unreacted silicone have to be removed in a time-consuming extraction process that would be extremely difficult to scale up.

25

A need exists for conveniently prepared and cost-effective polysiloxane block copolymers for use in cosmetics and personal care compositions.

30 The present invention provides an improved process for making polysiloxane block copolymers in which radical

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macroinitiators are prepared from organopolysiloxanes using a simple nucleophilic displacement reaction. The macroinitiators so produced may then be used in atom transfer radical polymerisation to prepare polysiloxane block copolymers of controlled architecture. Atom transfer radical polymerisation is described in general in *Polymer* Vol 39, No.21, pp 5163-5170 (Nakagawa et al) and used in WO98/51261 to make graft copolymers.

10 Summary of the Invention

In a first aspect, the present invention provides a process for making a polysiloxane block copolymer which is built up from units of the formula [A][B], in which A is a polymeric block built up from radically polymerisable monomer, and B is a polysiloxane block, the process comprising the steps of forming a polysiloxane macroinitiator by grafting a radical initiator onto a polysiloxane via a nucleophilic displacement reaction between groups on the polysiloxane and radical initiator respectively, and reacting the polysiloxane macroinitiator so obtained with radically polymerisable monomers in an atom transfer radical polymerisation reaction to form a polysiloxane block copolymer.

25

In a second aspect, the invention provides a polysiloxane block copolymer which is obtainable by the process described above.

- 5 -

The invention also provides a cosmetic and personal care composition, such as a hair styling composition, comprising the polysiloxane block copolymer as described above.

5 Detailed Description and Preferred Embodiments

Process

The process of the present invention comprises two key
10 reaction steps:

First reaction step

The first reaction step involves forming a polysiloxane
15 macroinitiator by grafting a radical initiator onto a polysiloxane via a nucleophilic displacement reaction between groups on the polysiloxane and radical initiator respectively.

20 Typically the polysiloxane macroinitiator is formed by a nucleophilic displacement reaction between:

(i) a polysiloxane which is end-capped with at least one
group capable of nucleophilic attack via its O ,N or S atom,
25
and

(ii) a radical initiator comprising at least one
- C (O) X group, in which X is a leaving group capable
30 substitution by the nucleophilic O ,N or S atom of polysiloxane (i), and at least one organic halide group

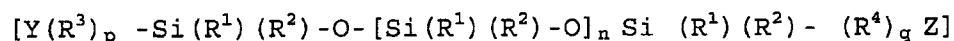
- 6 -

capable of generating a radical in the presence of a transition metal catalyst.

The polysiloxane (i) may be linear, branched or
5 hyperbranched, provided it is end-capped with at least one group as described above. By "end-capped" is meant that the group is at or near a terminal position of the polysiloxane.

Examples of preferred polysiloxanes have the formula:

10



in which n is an integer of 5 to 1,000,000;

15 R^1 and R^2 are independently selected from monovalent, optionally substituted, linear or branched C_{1-18} hydrocarbon radicals,

R^3 and R^4 are independently selected from divalent,
20 optionally substituted, linear or branched $C_1 - C_{18}$ hydrocarbon radicals;

p and q are integers having a value of 0 or 1, and

25 Y and Z are independently selected from hydroxyl, $-NH_2$ and $-NHR^5$ where R^5 is a monovalent, optionally substituted, linear or branched C_{1-18} hydrocarbon radical. Either, but not both, of Y and Z may also be hydrogen, or a monovalent, optionally substituted, linear or branched C_{1-18} hydrocarbon radical
30 thereby giving a mono-end-capped polysiloxane.

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Examples of monovalent, unsubstituted radicals are alkyl radicals, such as the methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl and tert-pentyl radical; alkoxy radicals, such as the methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, tert-butoxy, n-pentoxy, iso-pentoxy, neo-pentoxy and tert-pentoxy radical; hexyl radicals, such as the n-hexyl radical; alkenyl radicals, such as the vinyl, allyl, 5-hexenyl, 4-vinylcyclohexyl and the 3-norbornenyl radical; cycloalkyl radicals, such as cyclopentyl, cyclohexyl, 4-ethylcyclohexyl and cycloheptyl radical; norbornyl radicals and methylcyclohexyl radicals; aryl radicals, such as the phenyl, biphenyl, naphthyl, anthryl and phenanthryl radical; alkaryl radicals, such as o-, m- and p-tolyl radical, xylyl radicals and ethylphenyl radical; and aralkyl radicals, such as the benzyl, styryl, and phenylethyl radicals.

Examples of monovalent, substituted radicals are halogenated hydrocarbon radicals, such as the chloromethyl, 3-chloropropyl, 3-bromopropyl, 3,3,3-trifluoropropyl and 5,5,5,4,4,3,3-heptafluoropentyl radical and the chlorophenyl, dichlorophenyl and trifluorotolyl radical; mercaptoalkyl radicals, such as the 2-mercaptoethyl and 3-mercaptopropyl radical; cyanoalkyl radicals, such as the 2-cyanoethyl and 3-cyanopropyl radical; aminoalkyl radicals, such as the 3-aminopropyl, N-(2-aminoethyl)-3-aminopropyl and N-(2-aminoethyl)-3-amino-(2-methyl)propyl radical; aminoaryl radicals, such as the aminophenyl radical; acyloxyalkyl radicals, such as the 3-acryloxypropyl and 3-

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methacryloxypropyl radical; and hydroxyalkyl radicals, such as the hydroxypropyl radical.

Preferred monovalent radicals are independently selected
5 from unsubstituted or substituted C_1 to C_6 alkyl radicals or the phenyl radical, in particular the methyl, ethyl, propyl or phenyl radical.

Examples of divalent hydrocarbon radicals are linear or
10 branched saturated alkylene radicals, such as the methylene and ethylene radical, as well as propylene, butylene, pentylene, hexylene, cyclohexylene and octadecylene radicals; alkoxyalkylene radicals such as the methoxyethylene and ethoxyethylene radical; unsaturated
15 alkylene or arylene radicals, such as the hexenylene radical and phenylene radicals; alkarylene radicals such as the methylphenylene and ethylphenylene radical, and alkoxyarylene radicals such as the methoxyphenylene and ethoxyphenylene radical. The divalent hydrocarbon radical R^3
20 and R^4 can be interrupted by divalent radicals, bonded to carbon atoms on both sides, such as $-O-$, $-C(O)O-$, $-O(O)C-$, $-CONR^6-$, $-NR^6C(O)-$ and $-C(O)-$, where R^6 is hydrogen or a monovalent, optionally substituted, linear or branched C_{1-18} hydrocarbon radical as described above.

25

Particularly preferred polysiloxanes corresponding to the above general formula have:

30

$n = 5$ to $1,000,000$, preferably 5 to 500 ;

R^1 and $R^2 =$ methyl,

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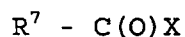
p and q = 0 and Y and Z = hydroxyl; or p and q = 1, R³ and R⁴ = (CH₂)₃ and Y and Z = NH₂.

The radical initiator (ii) comprises at least one

- 5 - C (O) X group, in which X is a leaving group capable of substitution by the nucleophilic O, N or S atom of polysiloxane (i), and at least one organic halide group capable of generating a radical in the presence of a transition metal catalyst.

10

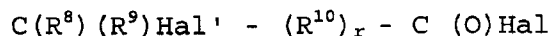
Examples of preferred radical initiators have the formula:



15

- where R⁷ is the organic halide group and X is the leaving group. Preferably X is a halogen atom (F, Cl, Br or I). By "organic halide group" is meant any linear, branched or cyclic (aromatic or otherwise) carbon structure, whether
20 substituted or unsubstituted, which also contains a halogen atom (F, Cl, Br or I).

Preferred radical initiators have the general formula:



25

- where Hal' and Hal independently denote halogen atoms, R⁸ and R⁹ are independently selected from hydrogen or a monovalent, optionally substituted, linear or branched C₁₋₁₈ hydrocarbon radical as described above, r is an integer having a value of
30 0 or 1, and R¹⁰ is selected from divalent, optionally

- 10 -

substituted, linear or branched $C_1 - C_{18}$ hydrocarbon radicals as described above.

A particularly preferred radical initiator corresponding to
5 the above general formula has:

Hal and Hal' = Br, R^8 and R^9 = methyl and $r = 0$.

The first reaction step involves a nucleophilic displacement
10 reaction between (i) and (ii) under conventional reaction conditions. The nucleophilic O, N or S atom of polysiloxane (i) replaces leaving group X of radical initiator (ii), thereby linking (i) and (ii) to generate a polysiloxane macroinitiator.

15

Second reaction step

The second reaction step involves reacting the organic halide groups of the polysiloxane macroinitiator obtained in
20 step (i) with radically polymerisable monomers in the presence of a catalytic or stoichiometric amount of a Cu (I) salt or other transitional metal species to form a polysiloxane block copolymer.

25 In this reaction step, the organic halide groups act as initiators in the presence of the radically polymerisable monomers and the catalyst, resulting in the linking of a block of radically polymerisable monomers onto the polysiloxane macroinitiator by atom transfer radical
30 polymerisation. This block of radically polymerisable

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monomers constitutes the polymeric block (denoted A) of the polysiloxane block copolymer as described above.

The catalyst for the second reaction step is a transition
5 metal salt, preferably a Cu(I) salt such as Cu(I) halide
salts (Cl, F, Br, I) and which is preferably complexed to a
ligand which is suitable for solubilising the Cu(I) salt in
the reaction mixture. WO98/51261 describes preferred ligands
for use in solubilising the Cu(I) salt in the reaction
10 mixture (aprotic bidentates such as diphosphates, 2,2'
bipyridyl, C₁-C₂₀ alkyl substituted bipyridyl and
combinations thereof, most preferably 2,2' bipyridyl
complexed to a Cu(I) halide salt, in particular CuCl).
WO98/51262 also refers to several journal articles which
15 describe examples of the polymerisation process (atom
transfer radical polymerisation) used in the second reaction
step of the process of the present invention. Further
examples of such descriptions can be found in *Polymer* Vol
39, No.21, pp 5163-5170 (Nakagawa et al) and *Macromolecules*
20 1997, 30, 2190-2193 (Haddleton et al). Those skilled in the
art would understand that a variety of other ligands can
also be employed.

The polymerisation process of the second reaction step can
25 be furnished in bulk, solution, emulsion and suspension, as
would be understood by those skilled in the art.

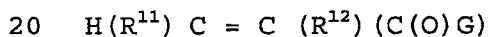
Radically polymerisable monomers suitable for use in the
second reaction step of the process of the present invention
30 are preferably ethylenically unsaturated monomers.

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By "polymerisable" is meant monomers that can be polymerised in accordance with the second reaction step of the process of the present invention using atom transfer radical polymerisation, more preferably "living" atom transfer radical polymerisation, in which polymer chain length and architecture can be controlled via stability of the radical, thus leading to improved monodispersity.

By "ethylenically unsaturated" is meant monomers that contain at least one polymerisable carbon-carbon double bond (which can be mono-, di-, tri- or tetra -substituted). Either a single monomer or a combination of two or more monomers can be utilised. In either case, the monomers are selected to meet the physical and chemical requirements of the final polysiloxane block copolymer.

Suitable ethylenically unsaturated monomers have the following general formula:



in which R^{11} and R^{12} are independently selected from hydrogen, $\text{C}_1 - \text{C}_{10}$ straight or branched chain alkyl, methoxy, ethoxy, 2-hydroxyethoxy, 2-methoxyethyl and 2-ethoxyethyl groups;

G is selected from hydroxyl, $-\text{O(M)}_{2/v}$, $-\text{OR}^{13}$, $-\text{NH}_2$, $-\text{NHR}^{13}$ and $-\text{N(R}^{13}\text{) (R}^{14}\text{)}$;

where M is a counter-ion of valency v selected from metal ions such as alkali metal ions and alkaline earth metal ions, ammonium ions and substituted ammonium ions such as

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mono-, di-, tri- and tetraalkylammonium ions, and each R^{13} and R^{14} is independently selected from hydrogen, C_1-C_8 straight or branched chain alkyl, N,N-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl.

- 5 Representative non-limiting examples of monomers useful herein include protected or non-protected acrylic acid and methacrylic acid and salts, esters and amides thereof.

The salts can be derived from any of the common nontoxic
10 metal, ammonium, or substituted ammonium counter ions. The esters can be derived from C_{1-40} straight chain, C_{3-40} branched chain, or C_{3-40} carbocyclic alcohols, from polyhydric alcohols having from about 2 to about 8 carbon atoms and from about 2 to about 8 hydroxyl groups (non-limiting examples of which
15 include ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, glycerol, and 1,2,6-hexanetriol); from amino alcohols (non-limiting examples of which include aminoethanol, dimethylaminoethanol and diethylaminoethanol and their quaternised derivatives); or from alcohol ethers
20 (non-limiting examples of which include methoxyethanol and ethoxyethanol).

The amides can be unsubstituted, N-alkyl or N-alkylamino mono-substituted, or N,N-dialkyl, or N,N-dialkylamino
25 disubstituted, wherein the alkyl or alkylamino groups can be derived from C_{1-40} straight chain, C_{3-40} branched chain, or C_{3-40} carbocyclic moieties. In addition, the alkylamino groups can be quaternised. Also useful as monomers are protected and unprotected acrylic or/and methacrylic acids,
30 salts, esters and amides thereof, wherein the substituents are on the two and three carbon position of the acrylic

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and/or methacrylic acids, and are independently selected from C₁₋₄ alkyl, hydroxyl, halide (-Cl, -Br, -F, -I), -CN, and -CO₂H, for example methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid and 3-cyano acrylic acid. The salts, esters, and amides of these substituted acrylic and methacrylic acids can be defined as described above for the acrylic/methacrylic acid salts, esters and amides. Other useful monomers include vinyl and allyl esters of C₁₋₄₀ straight chain, C₃₋₄₀ branched chain, or C₃₋₄₀ carbocyclic carboxylic acids, vinyl and allyl halides (e.g. vinyl chloride, allyl chloride), (e.g. vinyl pyridine, allyl pyridine); vinylidene chloride; and hydrocarbons having at least one unsaturated carbon-carbon double bond (e.g. styrene, alpha-methylstyrene, t-butylstyrene, butadiene, isoprene, cyclohexadiene, ethylene, propylene, 1-butene, 2-butene, isobutylene, p-methylstyrene); and mixtures thereof.

Preferred monomers useful herein include those selected from protected and unprotected acrylic acid, methacrylic acid, ethacrylic acid, methyl acrylate, ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, octyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, iso-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, decyl methacrylate, methyl ethacrylate, ethyl ethacrylate, n-butyl ethacrylate, iso-butyl ethacrylate, t-butyl ethacrylate, 2-ethylhexyl ethacrylate, decyl ethacrylate, 2,3-dihydroxypropyl acrylate, 2,3-dihydroxypropyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, hydroxypropyl methacrylate, glyceryl monoacrylate, glyceryl monoethacrylate, glycidyl

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methacrylate, glycidyl acrylate, acrylamide, methacrylamide, ethacrylamide, N-methyl acrylamide, N,N-dimethyl acrylamide, N,N-dimethyl methacrylamide, N-ethyl acrylamide, N-isopropyl acrylamide, N-butyl acrylamide, N-t-butyl acrylamide,

5 N,N-di-n-butyl acrylamide, N,N-diethylacrylamide, N-octyl acrylamide, N-octadecyl acrylamide, N,N-diethylacrylamide, N-phenyl acrylamide, N-methyl methacrylamide, N-ethyl methacrylamide, N-dodecyl methacrylamide, N,N-dimethylaminoethyl acrylamide, quaternised N,N-

10 dimethylaminoethyl acrylamide, N,N-dimethylaminoethyl methacrylamide, quaternised N,N-dimethylaminoethyl methacrylamide N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl methacrylate, quaternised N,N-dimethylaminoethyl acrylate, quaternised N,N-dimethylaminoethyl

15 methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl ethacrylate, glyceryl acrylate, 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, 2-methoxyethyl ethacrylate, 2-ethoxyethyl acrylate, 2-ethoxyethyl methacrylate, 2-ethoxyethyl ethacrylate, maleic

20 acid, maleic anhydride and its half esters, fumaric acid, itaconic acid, itaconic anhydride and its half esters, crotonic acid, angelic acid, diallyldimethyl ammonium chloride, vinyl pyrrolidone vinyl imidazole, methyl vinyl ether, methyl vinyl ketone, maleimide, vinyl pyridine, vinyl

25 furan, styrene sulphonate, allyl alcohol, allyl citrate, allyl tartrate, vinyl acetate, vinyl alcohol, vinyl caprolactam and mixtures thereof.

More preferred monomers are those selected from methyl

30 acrylate, methyl methacrylate, methyl ethacrylate, ethyl acrylate, ethyl methacrylate, ethyl ethacrylate, n-butyl

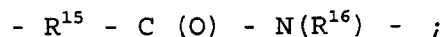
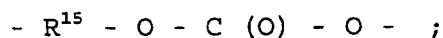
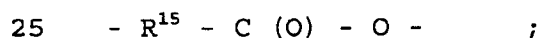
- 16 -

acrylate, n-butyl methacrylate, n-butyl ethacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, 2-ethylhexyl ethacrylate, N-octyl acrylamide, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate, N,N-dimethylaminoethyl acrylate,
 5 N,N-dimethylaminoethyl methacrylate, acrylic acid, methacrylic acid, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate and mixtures thereof.

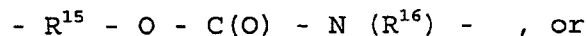
Most preferred monomers are those selected from N,N-
 10 dimethylaminoethyl acrylate, N,N-dimethylaminoethyl methacrylate, 2-ethylhexyl acrylate, hydroxyethyl methacrylate, N-octyl acrylamide, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate and mixtures thereof.

15 Polysiloxane Block Copolymers

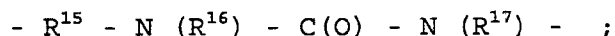
A typical polysiloxane block copolymer obtainable by the process described above is built up from units of the general formula [A]L[B], in which A is a polymeric block
 20 built up from radically polymerisable monomer, B is a polysiloxane block and L is a divalent linker group which links the A and B blocks via O-Si, N-Si or S-Si bonds to the B block. Preferably L is selected from:



30



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in which R^{15} is a divalent, optionally substituted, linear or branched $C_1 - C_{18}$ hydrocarbon radical as described above, and

5

R^{16} and R^{17} are independently selected from monovalent, optionally substituted, linear or branched C_{1-18} hydrocarbon radicals as described above.

- 10 The overall molecular architecture of the silicone block copolymers of the invention can be described by the formulas A-L-B, A-L-B-L-A, $-(A-L-B)_n-$, wherein n is an integer of 2 or greater, or $[A-L-][A-L-]B[-L-A][-L-A]$, wherein A-L-B represents a diblock structure, A-L-B-L-A represents a
- 15 triblock structure, $-(A-L-B)_n-$ represents a multiblock structure, and $[A-L-][A-L-]B[-L-A][-L-A]$ represents a dendritic structure.

Cosmetic and Personal Care Compositions

20

- The polysiloxane block copolymers of the present invention are preferably formulated into hair care compositions, especially hairspray compositions, but can also be formulated into a wide variety of product types, including
- 25 mousses, gels, lotions, tonics, sprays, shampoos, conditioners, rinses, hand and body lotions, facial moisturisers, sunscreens, anti-acne preparations, topical analgesics, mascaras, and the like. The carriers and additional components required to formulate such products
- 30 vary with product type and can be routinely chosen by one

- 18 -

skilled in the art. The following is a description of some of these carriers and additional components.

Carriers

5

Hair care compositions of the present invention can comprise a carrier, or a mixture of such carriers, which are suitable for application to the hair. The carriers are present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%, more preferably from about 10.0% to about 98.0%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to the underlying skin. Carriers suitable for use with hair care compositions of the present invention include, for example, those used in the formulation of hair sprays, mousses, tonics, gels, shampoos, conditioners, and rinses. The choice of appropriate carrier will also depend on the particular copolymer to be used, and whether the product formulated is meant to be left on the surface to which it is applied (e.g., hair spray, mousse, tonic, or gel) or rinsed off after use (e.g., shampoo, conditioner, rinse).

25 The carriers used herein can include a wide range of components conventionally used in hair care compositions. The carriers can contain a solvent to dissolve or disperse the particular copolymer being used, with water, the C1-C6 alcohols, lower alkyl acetate and mixtures thereof being preferred. The carriers can also contain a wide variety of additional materials such as acetone,

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hydrocarbons (such as isobutane, hexane, decene),
halogenated hydrocarbons (such as Freons) and volatile
silicon derivatives such as cyclomethicone. When the hair
care composition is a hair spray, tonic, gel, or mousse the
5 preferred solvents include water, ethanol, volatile silicone
derivatives, and mixtures thereof. The solvents used in such
mixtures may be miscible or immiscible with each other.
Mousses and aerosol hair sprays can also utilise any of the
conventional propellants to deliver the material as a foam
10 (in the case of a mousse) or as a fine, uniform spray (in
the case of an aerosol hair spray). Examples of suitable
propellants include materials such as
trichlorofluoromethane, dichlorodifluoromethane,
difluoroethane, dimethylether, propane, n-butane or
15 isobutane. A tonic or hair spray product having a low
viscosity may also utilise an emulsifying agent. Examples of
suitable emulsifying agents include nonionic, cationic,
anionic surfactants, or mixtures thereof. If such an
emulsifying agent is used, it is preferably present at a
20 level of from about 0.01% to about 7.5% of the composition.
The level of propellant can be adjusted as desired but is
generally from about 3% to about 30% of mousse compositions
and from about 15% to about 50% of the aerosol hair spray
compositions.
25
Suitable spray containers are well known in the art and
include conventional, non-aerosol pump sprays i.e.,
"atomisers", aerosol containers or cans having
propellant, as described above, and also pump aerosol
30 containers utilising compressed air as the propellant.

- 20 -

Where the hair care compositions are conditioners and rinses the carrier can include a wide variety of conditioning materials. Where the hair care compositions are shampoos, the carrier can include, for example, surfactants,
5 suspending agents, and thickeners.

The carrier can be in a wide variety of forms. For example, emulsion carriers, including oil-in-water, water-in-oil, water-in-oil-in-water, and oil-in-water-in-silicone
10 emulsions, are useful herein. These emulsions can cover a broad range of viscosities, e.g., from about 100 cps to about 200,000 cps. These emulsions can also be delivered in the form of sprays using either mechanical pump containers or pressurised aerosol containers using conventional
15 propellants. These carriers can also be delivered in the form of a mousse. Other suitable topical carriers include anhydrous liquid solvents such as oils, alcohols, and silicones (e.g., mineral oil, ethanol, isopropanol, dimethicone, cyclomethicone, and the like); aqueous-based
20 single phase liquid solvents (e.g., hydro-alcoholic solvent systems); and thickened versions of these anhydrous and aqueous-based single phase solvents (e.g., where the viscosity of the solvent has been increased to form a solid or semi-solid by the addition of appropriate gums, resins,
25 waxes, polymers, salts, and the like).

Additional Components

A wide variety of additional components can be employed in
30 cosmetic and personal care compositions according to the present invention. Examples include the following:

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- sunscreening agents such as 2-ethylhexyl
p-methoxycinnamate, 2-ethylhexyl N,N-dimethyl-p-
aminobenzoate, p-aminobenzoic acid, 2-phenylbenzimidazole-5-
sulfonic acid, octocrylene, oxybenzone, homomenthyl
5 salicylate, octyl salicylate, 4,4'-methoxy-t-
butyldibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-
benzylidene camphor, 3-(4-methylbenzylidene) camphor,
titanium dioxide, zinc oxide, silica, iron oxide, and
mixtures thereof.
- 10
- anti-dandruff actives such as zinc pyrithione,
piroctone olamine, selenium disulphide, sulphur, coal tar,
and the like.
- 15 - conditioning agents for hair care compositions such as
hydrocarbons, silicone fluids, and cationic materials. The
hydrocarbons can be either straight or branched chain and
can contain from about 10 to about 16, preferably from about
12 to about 16 carbon atoms. Examples of suitable
20 hydrocarbons are decane, dodecane, tetradecane, tridecane,
and mixtures thereof. Examples of suitable silicone
conditioning agents useful herein can include either cyclic
or linear polydimethylsiloxanes, phenyl and alkyl phenyl
silicones, and silicone copolyols. Cationic conditioning
25 agents useful herein can include quaternary ammonium salts
or the salts of fatty amines.
- surfactants for hair shampoo and conditioner
compositions. For a shampoo, the level is preferably from
30 about 10% to about 30%, preferably from 12% to about 25%, of
the composition. For conditioners, the preferred level of

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surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

5

- carboxylic acid polymer thickeners. These crosslinked polymers contain one or more monomers derived from acrylic acid, substituted acrylic acids, and salts and esters of these acrylic acids and the substituted acrylic acids, wherein the crosslinking agent contains two or more carbon-carbon double bonds and derived from a polyhydric alcohol. Examples of carboxylic acid polymer thickeners useful herein are those selected from the group consisting of carbomers, acrylates/C10-C30 alkyl acrylate crosspolymers, and mixtures thereof. Compositions of the present invention can comprise from about 0.025% to about 1%, more preferably from about 0.05% to about 0.75% and most preferably from about 0.10% to about 0.50% of the carboxylic acid polymer thickeners.

20

- emulsifiers for emulsifying the various carrier components of the compositions of the invention. Suitable emulsifier types include polyethylene glycol 20 sorbitan monolaurate (Polysorbate 20), polyethylene glycol 5 soya sterol, Steareth-20, Cetareth-20, PPG-2 methyl glucose ether distearate, Ceteth-10, Polysorbate 80, cetyl phosphate, potassium cetyl phosphate, diethanolamine cetyl phosphate, Polysorbate 60, glyceryl stearate, PEG-100 stearate, and mixtures thereof. The emulsifiers can be used individually or as a mixture of two or more and can comprise from about 0.1% to about 10%, more preferably from about 1%

30

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to about 7%, and most preferably from about 1% to about 5% of the compositions of the present invention.

- vitamins and derivatives thereof (e.g., ascorbic acid,
5 vitamin E, tocopheryl acetate, retinoic acid, retinol, retinoids, and the like.

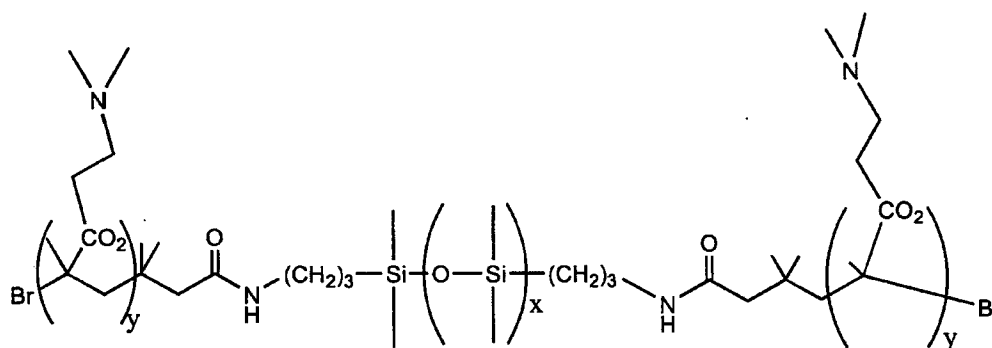
- cationic polymers (e.g., cationic guar gum derivatives such as guar hydroxypropyltrimonium chloride and
10 hydroxypropyl guar hydroxypropyltrimonium chloride, available as the Jaguar C series from Rhone-Poulenc).

- preservatives, antioxidants, chelators and sequestrants; and aesthetic components such as fragrances, colourings,
15 hair nutrients and essential oils.

The invention will now be illustrated by the following non-limiting Examples:

EXAMPLESExamples 1-8

- 5 ABA Triblock copolymers of the following general formula:



PDMAEMA-PDMS-PDMAEMA ABA TRIBLOCK

- 10 were prepared by atom transfer radical polymerisation (ATRP). Commercially available polydimethyl siloxanes (PDMS) - amine propyl terminated were halide functionalised to give an effective ATRP initiator. Controlled molecular weights were achieved with narrow polydispersities.

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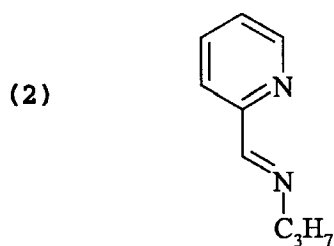
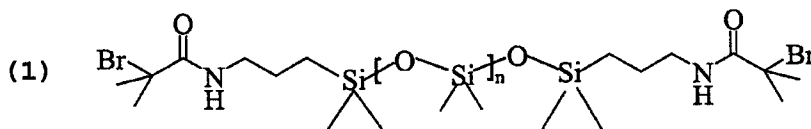
EXAMPLE	Mwt of Initiator	Value of x	Mwt of DMAEMA	Value of y	Total Mwt of Polymer
1	3300	45	10000	64	13300
2	3300	45	4000	25	7300
3	3300	45	6000 (NMR)	40	9300
4	2000	27	15000 (NMR)	95	17000
*5	800	7	10000	64	10800
6	3300	45	4700 (NMR)	30	8000
*7	800	7	10000	64	10800
8	3300	45	10000	64	13300

*Examples 5 and 7 were prepared using an ester PDMS initiator rather than the pictured amide PDMS initiator, giving an - O - linkage in place of the pictured
 5 - (CH₃)₂ -NH- linkage in the final polymer.

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Preparation Method

Cu^IBr (0.2732g, 1.905mmol) along with a magnetic stirrer bar was placed in a dry Schlenk flask which was then evacuated and flushed with nitrogen three times. 2-dimethylaminoethyl methacrylate (3.9mL, 0.023moles), toluene (7.2mL) and the PDMS initiator (1) (2g, 0.952mmol) were added to the Schlenk using degassed syringes.* The solution was then deoxygenated by three freeze-pump-thaw cycles. Finally, once the flask had reached the desired reaction temperature of 90°C the n-propyl-2-pyridinalmethanimine ligand (2) (0.54mL, 3.809mmol) was added with stirring. The reaction mixture immediately turned dark brown in colour on addition of the ligand.



*Target molecular weight of DMAEMA blocks = 4000, molecular weight of initiator = 2000 (total = 6000). The ratio of [monomer] : [initiator] determines molecular weight of end polymer. In the described ATRP the required ratio of

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[monomer] : [initiator] = 25 : 1. The ratios for the other listed reagents are as follows; $[\text{Cu}^{\text{I}}\text{Br}]$: [Initiator] = 1:2, [Ligand] : $[\text{Cu}^{\text{I}}\text{Br}]$ = 2:1 and solvent volume : monomer volume = 2:1.

5

The monomer was purified by passing down a basic alumina column prior to use and purged with nitrogen for at least one hour. Toluene, which was used as a solvent for all polymerisations, was also degassed in this manner. $\text{Cu}^{\text{I}}\text{Br}$ was
10 purified before use according to a published procedure.¹

1) Keller, R. N.; Wycoff, H. D. *Inorganic Synthesis*, 1947, 2,1.

15 Purification of polymer

The resultant dark brown solution was passed down an alumina column several times using a conventional solvent such as dichloromethane or tetrahydrofuran. When the solution
20 appeared colourless the solvent was removed under vacuum to yield a pale yellow solid.

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ResultsFilm Forming

- 5 A solution of ethanol / water (55%:45%) was made up. A small sample of polymer (0.5g) was added to the solution (10 mL). Some samples needed agitation but others dissolved straight away. A small quantity of solution (1mL) was placed in a plastic dish and left to dry for 3 hours.

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EXAMPLE	FILM FORMING PROPERTIES	SOLUBILITY			
		100% water	100% ethanol	55% ethanol/water	100% Methyl Acetate
1	non tacky clear flexible	soluble	soluble	soluble	soluble
2	slightly yellow non tacky flexible	soluble	soluble	soluble	soluble
3	non tacky clear flexible	soluble	soluble	soluble	soluble
4	non tacky clear flexible	soluble	soluble	soluble	soluble
5	non tacky clear flexible	soluble	soluble	soluble	soluble
6	slightly yellow non tacky flexible	soluble	soluble	soluble	soluble
7	slightly yellow non tacky brittle	soluble	soluble	soluble	insoluble
8	slightly yellow non tacky brittle	soluble	soluble	soluble	insoluble

Bond strength analysis

5

Diastron MTT600 parameters: % extension = 100
 Rate (mm/min) = 10
 Max force(g) = 200
 Gauge force(gmf) = 2

- 30 -

5% aqueous alcohol solution (55% ethanol/water):

1 microlitre pipetted onto junction

Temperature = 20°C

5 Humidity = 50%

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EXAMPLE	BOND STRENGTH (g)	EXTENSION (%)
1	36.88 50.88 20.88 AVE = 42.53g 50.63 ST.DEV = 13.7 53.38	2.79 6.89 4.19 AVE = 6.76% 10.27 ST.DEV = 2.9 7.68
2	29.25 * * AVE = 26.29g 23.75 ST.DEV = 2.77 25.88	2.23 AVE = 2.45% 2.58 ST.DEV = 0.19 2.55
3	31.38 * * AVE = 31.42g 30.38 ST.DEV = 1.06 32.50	4.14 AVE = 4.17% 4.60 ST.DEV = 0.42 3.76
4	* 20.50 27.50 AVE = 25.78 29.88 ST.DEV = 4.00 25.25	2.83 4.77 AVE = 3.79% 4.75 ST.DEV = 1.12 2.82

5

10

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EXAMPLE	BOND STRENGTH (g)	EXTENSION (%)
5	56.00 26.00 45.25 AVE = 42.42g 43.88 ST.DEV = 15.20 40.38	6.23 3.21 5.55 AVE = 5.00% ST.DEV = 1.58
6	* * 7.5 AVE = 11.96g 16.63 ST.DEV = 4.56 11.75	1.89 AVE = 1.57 % 1.59 ST.DEV = 0.33 1.24
7	* * 24.13 AVE = 19.50g 22.00 ST.DEV = 6.26 12.38	4.73 AVE = 3.41% 3.24 ST.DEV = 1.25 2.25
8	* * 10.63 AVE = 14.79g 23.50 ST.DEV = 7.54 12.38	1.26 AVE = 1.61% 2.60 ST.DEV = 0.87 0.96

Sensory

5

The polymer of Example 1 was formulated into a 55% VOC
pumpspray(4.2% resin , 55% ethanol, 40.8% water)

This was sprayed on to a switch and compared against the
commercial product Suave ® Extra Hold(4.2% AMPHOMER ®)

10 pumpspray.

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The formulation with Example 1 had major wins on softness and least deposits(both before and after brushout).

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CLAIMS

1. A process for making a polysiloxane block copolymer which is built up from units of the formula [A] [B], in which A is
5 a polymeric block built up from radically polymerisable monomer, and B is a polysiloxane block, the process comprising the steps of forming a polysiloxane macroinitiator by grafting a radical initiator onto a polysiloxane via a nucleophilic displacement reaction
10 between groups on the polysiloxane and radical initiator respectively, and reacting the polysiloxane macroinitiator so obtained with radically polymerisable monomers in an atom transfer radical polymerisation reaction to form a polysiloxane block copolymer.
- 15
2. A process according to claim 1, comprising the steps of:
- (a) forming a polysiloxane macroinitiator by a nucleophilic substitution reaction between:
- 20
- (i) a polysiloxane which is end-capped with at least one group capable of nucleophilic attack via its O, N or S atom,
- and
- 25
- (ii) a radical initiator comprising at least one - C (O) X group, in which X is a leaving group capable of substitution by the nucleophilic O, N or S atom of polysiloxane (i), and at least one organic halide group
30 capable of generating a radical in the presence of a transition metal catalyst;

- 35 -

followed by

(b) reacting the organic halide groups of the polysiloxane macroinitiator so obtained with radically polymerisable monomers in the presence of a catalytic amount of a Cu (I) salt or other transitional metal species to form a polysiloxane block copolymer.

3. A polysiloxane block copolymer obtainable by the process of claim 1 or 2.

4. A polysiloxane block copolymer according to claim 3, which is built up from units of the general formula [A]L[B], in which A is a polymeric block built up from radically polymerisable monomer, B is a polysiloxane block and L is a divalent linker group which links the A and B blocks via O-Si, N-Si or S-Si bonds to the B block, and which is preferably selected from:

- R¹⁵ - C (O) - O - ;

- R¹⁵ - O - C (O) - O - ;

- R¹⁵ - C (O) - N(R¹⁶) - ;

- R¹⁵ - O - C(O) - N (R¹⁶) - , or

- R¹⁵ - N (R¹⁶) - C(O) - N (R¹⁷) - ;

in which R¹⁵ is a divalent, optionally substituted, linear or branched C₁ - C₁₈ hydrocarbon radical, and

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R¹⁶ and R¹⁷ are independently selected from monovalent, optionally substituted, linear or branched C₁₋₁₈ hydrocarbon radicals.

5 5. A cosmetic and personal care composition comprising the polysiloxane block copolymer of claim 3 or 4.

6. A cosmetic and personal care composition according to claim 5, which is formulated as a hairspray, gel or mousse.

10

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/04225

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G77/42 C08G77/442 C08F283/12 C08F293/00 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C08F A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>NAKAGAWA Y ET AL: "Development of novel attachable initiators for atom transfer radical polymerization. Synthesis of block and graft copolymers from poly(dimethylsiloxane) macroinitiators" POLYMER,GB,ELSEVIER SCIENCE PUBLISHERS B.V.,</p> <p>vol. 39, no. 21,</p> <p>1 October 1998 (1998-10-01), pages 5163-5170, XP004139649</p> <p>ISSN: 0032-3861</p> <p>cited in the application</p> <p>page 5163, left-hand column, paragraph 1</p> <p>-page 5169, left-hand column, paragraph 3;</p> <p>figures; examples</p> <p>----</p> <p>-/--</p>	1-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

20 July 2000

Date of mailing of the international search report

31/07/2000

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INTERNATIONAL SEARCH REPORT

Int lional Application No

PCT/EP 00/04225

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98 01480 A (UNIV CARNEGIE MELLON) 15 January 1998 (1998-01-15) page 35, line 11 -page 38, line 20; examples 14-16,19,23,24 ---	1-6
Y	WO 98 51261 A (PROCTER & GAMBLE) 19 November 1998 (1998-11-19) cited in the application the whole document -----	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No

PCT/EP 00/04225

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9801480 A	15-01-1998	US 5789487 A	04-08-1998
		AU 3585997 A	02-02-1998
		BR 9710273 A	10-08-1999
		CA 2259995 A	15-01-1998
		CN 1228789 A	15-09-1999
		EP 0914352 A	12-05-1999
		US 5945491 A	31-08-1999
WO 9851261 A	19-11-1998	AU 7073798 A	08-12-1998
		EP 0977540 A	09-02-2000
		ZA 9804087 A	16-11-1998

(19) World Intellectual Property Organization
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(54) Title: POLYMERS, THEIR PRECURSORS AND PROCESSES FOR PREPARATION THEREOF

(57) Abstract: Novel block polymers of ethylenically unsaturated monomers and ethylenically unsaturated carboxylates such as vinyl acetate may be made by transition metal mediated, atom transfer polymerisation of an ethylenically unsaturated monomer with an α , ω di-functional polymer precursor having repeating units derived from an ethylenically unsaturated carboxylate, such as vinyl acetate. Also, novel α , ω di-functional polymer precursors may be made by the steps of (a) reacting an ethylenically unsaturated carboxylate with a radical initiator having a substitutable functional group; and (b) substituting the functional groups on the product of step (a) with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.

POLYMERS, THEIR PRECURSORS AND PROCESSES FOR PREPARATION
THEREOF

The present invention relates to a process for preparing polymers, novel polymers, a process for preparing polymer precursors and novel polymer precursors.

The preparation of polymers by transition metal mediated, atom transfer polymerisation processes is known, see for example K. Matyjaszewski in '*Controlled*
5 *Radical Polymerisation*', American Chemical Society, 1998. Transition metal mediated, atom transfer polymerisation processes involve the polymerisation of a monomer in the presence of (i) a transition metal in a low valency state, usually present as the halide, preferably chloride or bromide, (ii) an organodiimine and (iii) an initiator compound comprising a homolytically cleavable bond with a halogen atom.

10 Wang J-S et al in *Macromolecules* 1995, 28, 7901-7910 describe an atom transfer polymerisation process using an alkyl halide R-X (X= Cl and Br) and a transition metal species complexed by suitable ligand(s) M_t^n/L_x such as $CuX/2,2'$ -bipyridine for the polymerisation of styrenes and (meth)acrylates.

International Patent Publication WO97/47661 describes a process for the atom
15 transfer polymerisation of olefinically unsaturated monomers in the presence of (i) a transition metal such as copper, (ii) an organodiimine wherein at least one of the nitrogens of the diimine is not part of an aromatic ring such as a 1,4-diaza-1,3-butadiene, a pyridinecarbaldehyde, an oxazolidone or a quinoline carbaldehyde and (iii) an initiator compound comprising a homolytically breakable bond with a halogen atom.

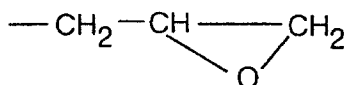
20 It has now been found that block co-polymers of ethylenically unsaturated carboxylates such as vinyl acetate, with ethylenically unsaturated monomers such as

styrene, acrylates and methacrylates can be prepared by transition metal mediated, atom transfer polymerisation.

According to a first aspect of the present invention there is provided a process for the preparation of a block polymer which process comprises a transition metal mediated, atom transfer polymerisation of an ethylenically unsaturated monomer with an α, ω di-functional polymer precursor having repeating units derived from an ethylenically unsaturated carboxylate. A preferred ethylenically unsaturated carboxylate is vinyl acetate. Such block polymers are believed to be of the ABA type.

According to this aspect of the present invention, the transition metal mediated, atom transfer polymerisation may be preformed in the presence of (i) a first component represented by MY where M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand and Y is a monovalent or polyvalent counterion, (ii) an organodiimine, (iii) the α, ω di-functional polymer precursor and (iv) an ethylenically unsaturated monomer.

The ethylenically unsaturated monomer may be : styrene; acrylonitrile; methacrylonitrile; acrylamide; methacrylamide; acrylic acid; unsubstituted acrylate for example having a formula $H_2C=CH-CO_2Z$ in which Z is methyl, allyl, or a functional group such as $-CH_2CH_2OH$ or $-CH_2CH_2N(CH_3)_2$; or a methacrylate for example having a formula $H_2C=C(CH_3)-CO_2Z'$ in which Z' is H, methyl, allyl, benzyl, or a functional group such as $-CH_2CH_2OH$, $-CH_2CH_2N(CH_3)_2$, $-CH_2-CH=CH_2$, $-CH_2NH_3^+Cl^-$ or



In the first component represented by MY, M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand and Y is a monovalent or polyvalent counterion. Suitable transition metals, M may be Cu(I), Fe(II), Co(II), Ru(II) and Ni(II), preferably, Cu(I). The non-charged ligand may be CH_3CN . Y may be chosen from Cl, Br, F, I, NO_3 , PF_6 , BF_4 , SO_4 , CN, SPh, SCN, SePh or triflate (CF_3SO_3).

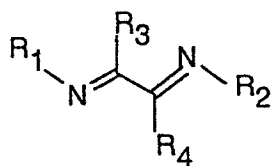
Suitably, the transition metal component and the organodiimine are present as a complex represented by the formula $[ML_m]^{n+} A^{n-}$ wherein M is a transition metal in a low

valency state; L is an organodiimine; A^{n-} is an anion; n is an integer of 1 to 3; and m is an integer of 1 to 2. Suitable transition metals M, may be Cu(I), Fe(II), Co(II), Ru(II) and Ni(II), preferably, Cu(I). Suitably, A represents Cl, Br, F, I, NO_3 , PF_6 , BF_4 , SO_4 , CN, SPh, SCN, SePh or triflate (CF_3SO_3). Most preferably, as $[ML_m]^{n+} A^{n-}$ there is used

5 CuBr.

The organodiimine may be :

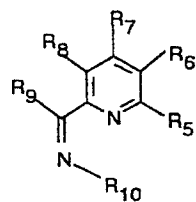
a 1,4-diaza-1,3-butadiene such as represented by Formula (1) :



10

Formula (1)

a 2-pyridinecarbaldehyde imine such as represented by the Formula (2) :

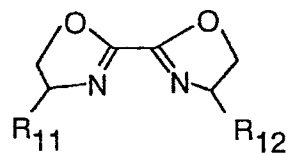


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Formula (2)

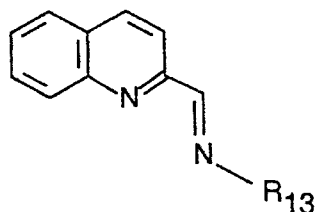
an oxazolidone such as represented by Formula (3) :

20



Formula (3)

or a quinoline carbaldehyde such as represented by Formula (4) :



5

Formula (4)

- wherein R_1 , R_2 , R_{10} , R_{11} , R_{12} , and R_{13} may be varied independently and R_1 , R_2 , R_{10} , R_{11} , R_{12} and R_{13} may be H, straight chain, branched chain or cyclic saturated alkyl, hydroxyalkyl, carboxyalkyl, aryl (such as phenyl or substituted phenyl where substitution is as described for R_4 to R_9), CH_2Ar (where Ar = aryl or substituted aryl) or a halogen. Preferably, R_1 , R_2 , R_{10} , R_{11} , R_{12} , and R_{13} may be a C_1 to C_{20} alkyl, hydroxyalkyl or carboxyalkyl in particular C_1 to C_4 alkyl, especially methyl or ethyl, n-propyl, isopropyl, n-butyl, *sec*-butyl, *tert*. butyl, cyclohexyl, 2-ethylhexyl, octyl, decyl or lauryl. R_1 , R_2 , R_{10} , R_{11} , R_{12} , and R_{13} may especially be methyl.

R_3 to R_9 may independently be selected from the group described for R_1 , R_2 , R_{10} , R_{11} , R_{12} , and R_{13} and OCH_{2n+1} (where n is an integer from 1 to 20), NO_2 , CN, and $O=CR$ (where R = alkyl, benzyl $PHCH_2$ or a substituted benzyl, preferably a C_1 to C_{20} alkyl, especially a C_1 to C_4 alkyl).

- The organodiimine may exhibit a chiral centre α to one of the nitrogen groups. Compounds of Formula (2) may comprise one or more fused rings on the pyridine group.

One or more adjacent R_1 and R_3 , R_3 and R_4 , R_4 and R_2 , R_{10} and R_9 , R_8 and R_9 , R_3 and R_7 , R_7 and R_6 , R_6 and R_5 groups may be C_5 to C_8 cycloalkyl, cycloalkenyl, polycycloalkyl, polycycloalkenyl or cyclicaryl, such as cyclohexyl, cyclohexenyl or norbornenyl.

Preferred organodiimines include compounds represented by Formula (2) in which $R_5 = R_6 = R_7 = R_8 = R_9 = H$ and R_{10} is selected from the group consisting of : C_2H_5- , $n-C_3H_7-$, $(CH_3)_2CH-$, $cycloC_3H_5-$, $n-C_5H_{11}-$, $n-C_6H_{13}-$, $n-C_7H_{15}-$, $n-C_8H_{17}-$, $n-C_9H_{19}-$, $n-C_{18}H_{37}-$, $CH_3(C_2H_5)CH-CH_2-$, $HO-CH_2-CH_2-$, $HO-CH_2-CH_2-CH_2-$,

HC*(CH₃)Ph (R form), HC*(CH₃)Ph (S form), HC*(CH₃)Ph (RS form), HO₂CCH₂- and HO₂CC*H(R₁₄)- wherein * indicates a chiral centre, Ph is a phenyl group and R₁₄ is hydrogen, C₁ to C₁₀ branched alkyl, carboxy- or hydroxy- C₁ to C₁₀ alkyl. Preferred organodiimines represented by Formula (2) include n-propyl-pyridinal methanimine and
 5 n-octyl-pyridinal methanimine.

Other suitable catalyst systems for the atom transfer polymerisation included :

- (I) RuCl₂(PPh₃)₃/CCl₄/methylaluminium bis-(2,6-di-*tert*-butylphenoxide); NiBr₂(PPh₃)₂, NiBr₂(P*n*Bu₃)₂; and FeCl₂(PPh₃)₂ being described in *Macromolecules* 1995, 28, 1721; *Macromolecules* 1997, 30, 2249; and
 10 *Macromolecules* 1997, 30, 4507, the contents of which are hereby incorporated by reference;
- (II) Cu(I)Br/ligand/initiator/monomer/solvent in which the initiator is RX, methyl 2-bromopropionate, ethyl 2-bromopropionate, 1-phenylethyl bromide or ethyl 2-bromoisobutyrate and the ligand is a derivative of 2,2'-bipyridine or simple
 15 aliphatic polyamines, being described in *Macromolecules* 1999, 32, 290 and 1767; *Macromolecules* 1997, 30, 7967; *Macromolecules* 1995, 28, 7901; and J. Am. Chem. Soc. 1995, 117, 5614 the contents are hereby incorporated by reference.
- (III) [Ni{o,o'-(CH₂-NMe₂)₂C₆H₃}Br] with an initiator of CCl₄, 2-bromoisobutylphenone or 2-bromoethylisobutrate, being described in
 20 *Macromolecules* 1996, 29, 8576, the contents of which are hereby incorporated by reference.
- (IV) RhCl(PPh₃)₃ with dichloroacetophenone and 7 equivalents of triphenylphosphine, being described in *Macromolecules* 1998, 31, 542, the contents of which are
 25 hereby incorporated by reference.
- (V) [Pd(OAc)₂] with carbon tetrachloride and triphenylphosphine, being described in *Macromolecules* 1997, 30, 7631, the contents of which are hereby incorporated by reference.
- (VI) Cu(I)Cl/2,2'-bipyridine with arenesulfonyl chlorides being described in
 30 *Macromolecules* 1995, 28, 7970, the contents of which are hereby incorporated by reference.

The transition metal, mediated atom transfer polymerisation process may be preformed using conditions known in the art, for example such as described in International patent publication WO 97/47661, the contents of which are hereby incorporated by reference.

5 The atom transfer polymerisation process may be performed either using a solvent or in bulk, preferably in bulk due to the formation of gels. Non protic solvents may be used. Suitable solvents include hydrocarbons, anisole, ethyl acetate, diphenyl ether, higher alcohols, water and ketones such as acetone. Preferred solvents are xylene and toluene.

10 The atom transfer polymerisation process generally requires elevated temperature and this depends upon the catalyst system and monomers used. In particular, the polymerisation may be performed at a temperature in the range of -40°C to $+180^{\circ}\text{C}$, preferably 0°C to 150°C , more preferably in the range 10° to 130°C . Suitably 90°C may be used, although 110°C may be used for styrene co-polymerisation.

15 The polymerisation process is suitably performed at atmospheric pressure, although a higher pressure might be used.

In the polymerisation process, the molar ratio of ethylenically unsaturated monomer : α , ω di-functional polymer precursor initiator is suitably (3 to 100000) : 1, preferably (10 to 1000) : 1 more preferably (10 to 500) : 1.

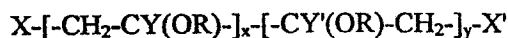
20 In the polymerisation process, the molar ratio of organodiimine ligand : transition metal is suitably (100 to 0.1) : 1, preferably (3 to 1) : 1.

In the polymerisation process, the molar ratio of α , ω di-functional polymer precursor initiator : transition metal is suitably (1000 to 0.01) : 1, preferably (10 to 0.5) : 1.

25 In the polymerisation process the concentration of monomer is suitably in the range 1 to 100 %, preferably in the range 20 to 50 % .

The α , ω di-functional polymer precursor acts as an initiator for the transition metal, atom transfer polymerisation process.

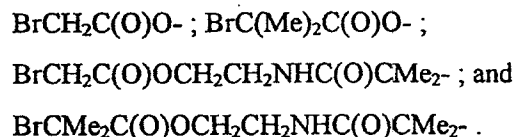
30 The α , ω di-functional polymer precursor may be a polymer precursor having a molecular weight in the range from 500 to 50000, preferably from 1000 to 20000 and being represented by the formula :



wherein x and y are integers independently greater than 1; Y and Y' are independently H or -CH₃; R represents a hydrocarbonyl group; and X and X' independently represent substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.

R may be selected from the group consisting of: CH₃C(O)-, Y"-C(O)-, PhC(O)-, Ph-, PhCH₂-, CH₃-(CH₂-CH₂-CH₂-CH₂)_zC(O)-, CH₃-(CH₂-CH=CH-CH₂)_z-C(O)- and substituted phenyl; wherein Y" is an n-alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z" is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent selected from the group consisting of NO₂, OMe, CN, NMe₂, OH, Cl, Br, and F. Preferably, R is CH₃C(O)-.

The X and X' groups preferably have homolytically cleavable Cl and/or Br bonds. Preferably, X and X' are independently selected from the group consisting of:



wherein Me represents CH₃-.

Such novel polymer precursors may be prepared by the steps (a) and (b) of the process hereinafter described and may be used in a transition metal mediated, atom transfer polymerisation for the preparation of block co-polymers of ethylenically unsaturated carboxylates such as vinyl acetate, with ethylenically unsaturated monomers such as styrene, (meth)acrylates, (meth)acrylonitriles and (meth)acrylamides.

Thus, according to another aspect of the present invention there is provided a process for the production of an α, ω di-functional polymer precursor which process comprises the steps of:

- (a) reacting an ethylenically unsaturated carboxylate with a radical initiator having a substitutable functional group; and
- (b) substituting the functional groups on the product of step (a) with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.

Preferably, the ethylenically unsaturated carboxylate is vinyl acetate optionally with other co-monomers known in the art.

Preferably, the radical initiator has a functional group selected from hydroxyl, carboxylic acid and amides, preferably hydroxyl. Suitably, the radical initiator having a hydroxyl function group is selected from hydrogen peroxide, azobis compounds having hydroxyl or amide functional groups and benzoyl peroxide. Suitable azobis compounds are:

- 4,4'-azobis (4-cyanopentanoic acid),
- 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]-propionamide},
- 10 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-ethyl]-propionamide} , and
- 2,2 - azobis(isobutyramide) dihydrate.

The reaction between the ethylenically unsaturated carboxylate with a radical initiator having a substitutable functional group in step (a) may be performed using conventional free radical polymerisation conditions, known in the art.

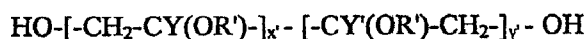
15 In step (b) the functional groups on the product of step (a) are substituted with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process. Preferably, such substituents have chlorine or bromine substituents α to an electron withdrawing activating group. Preferably, the electron withdrawing group of the substituent active for the formation of block polymers
20 in a transition metal mediated, atom transfer polymerisation process is selected from nitrile, ester and phenyl.

Preferably, in step (b) the product from step (a) is reacted with $\text{BrC}(\text{CH}_3)_2\text{C}(\text{O})\text{Br}$.

In step (b) the functional groups on the product of step (a) may be substituted
25 with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process under conventional conditions known in the art. Thus a reaction temperature of 0°C or room temperature may be used, depending upon the exotherm. Atmospheric pressure may suitably be used. Dry solvents are used, for example THF, pyridine and toluene. The brominating agent is
30 added in excess. Hydrogen bromide formed in the reaction may be removed, for example by precipitation as $\text{HBr} \cdot \text{NEt}_3$ with triethylamine.

The novel α, ω di-functional polymer precursors prepared according to this aspect of the present invention may be used in a transition metal mediated, atom transfer polymerisation for the preparation of block co-polymers of ethylenically unsaturated carboxylates such as vinyl acetate, with ethylenically unsaturated monomers such as
 5 styrene, (meth)acrylates, (meth)acrylonitriles and (meth)acrylamides.

According to a further aspect of the present invention there is provided a polymer precursor having a molecular weight in the range from 500 to 50000, preferably from 1000 to 20000 and being represented by the formula :



10 wherein x' and y' are integers independently greater than 1; Y and Y' are independently H or $-\text{CH}_3$; and R' represents a hydrocarbyl group.

R' may be selected from the group consisting of: $\text{CH}_3\text{C}(\text{O})-$, $\text{Y}''-\text{C}(\text{O})-$, $\text{PhC}(\text{O})-$, Ph-, PhCH_2- , $\text{CH}_3-(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-)_{z'}\text{C}(\text{O})-$, $\text{CH}_3-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-)_{z'}\text{C}(\text{O})-$ and substituted phenyl; wherein Y'' is an n-alkyl
 15 group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z'' is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent selected from the group consisting of NO_2 , OMe, CN, NMe_2 , OH, Cl, Br, and F. Preferably, R' is $\text{CH}_3\text{C}(\text{O})-$.

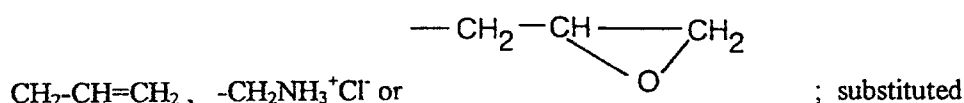
Such novel polymer precursors may be prepared by step (a) and used in step (b)
 20 of the process hereinbefore described.

According to yet a further aspect of the present invention there is provided a block polymer comprising alternating repeating units of $[-\text{A}-]$ and $[-\text{B}-]$ in which :
 $-\text{A}-$ represents a polymer block having a molecular weight in the range from 500 to 50000, preferably from 1000 to 20000 and being represented by the formula :



wherein x'' and y'' are integers independently greater than 1; Y and Y' are independently H or $-\text{CH}_3$ and R'' represents a hydrocarbyl group; and

$-\text{B}-$ represents at least one polymer repeating unit selected from the group consisting of acrylic; substituted acrylic for example, having a formula $-\text{HC}-\text{C}(\text{CO}_2\text{Z})-$ in which Z in
 30 which Z is methyl, allyl, or a functional group such as $-\text{CH}_2\text{CH}_2\text{OH}$ or $-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$; methacrylic for example, having a formula $-\text{HC}-\text{C}(\text{CH}_3)(\text{CO}_2\text{Z}')$ in which Z' is H, methyl, allyl, benzyl, or a functional group such as $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$, -



methacrylic; acrylonitrile; methacrylonitrile; acylamide; methacrylamide and styrenic polymer repeating units and is preferably at least one methacrylic, styrenic and/or n-butyl methacrylic repeating unit.

- 5 R" may be selected from the group consisting of: CH₃C(O)-, Y"-C(O)-, PhC(O)-, Ph-, PhCH₂-, CH₃-(CH₂-CH₂-CH₂-CH₂)_z-C(O)-, CH₃-(CH₂-CH=CH-CH₂)_z-C(O)- and substituted phenyl; wherein Y" is an n-alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z" is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent
- 10 selected from the group consisting of NO₂, OMe, CN, NMe₂, OH, Cl, Br, and F. Preferably, R" is CH₃C(O)-.

- The invention will now be described by reference to the following examples and with reference to Figures 1 to 23 in which Figures 1 (a) to (d) are NMR spectra data, Figure 2 is IR spectra data, Figure 3 is GPC data and Figure 4 is DSC data of polymer
- 15 precursor II according to the present invention; Figures 5 (a) to (d) are NMR spectra data, Figure 6 is IR spectra data and Figure 7 is GPC data of polymer precursor III according to the present invention; Figures 8 (a) to (d) are NMR spectra data, Figure 9 is IR spectra data, Figure 10 is GPC data of polymer precursor IV according to the present invention; Figure 11 is GPC data and Figure 12 is DSC data of polymer prepared in
- 20 Example 6 (a) according to the present invention; Figure 13 is GPC data, Figure 14 is DSC data and Figure 15 is NMR spectra data of polymer prepared in Example 6 (b) according to the present invention; Figure 16 is GPC data, Figure 17 is DSC data and Figure 18 is NMR spectra data of polymer prepared in Example 6 (c) according to the present invention; Figure 19 is GPC data and Figure 20 is NMR spectra data of polymer
- 25 prepared in Example 6 (d) according to the present invention; and Figure 21 is GPC data, Figure 22 is DSC data and Figure 23 is NMR spectra data of polymer prepared in Example 6 (e) according to the present invention.

Preparation of Polymer Precursors

Example 1 : Preparation of Polymer Precursor I

- 30 HO(CH₂CH(OAc))_x(CH(OAc)CH₂)_yOH

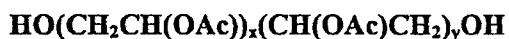
This illustrates step (a) of the polymer precursor preparation process according to the present invention.

Vinyl acetate and 1-propanol were deoxygenated by a stream of nitrogen for at least 30 minutes immediately prior to use. A mixture of vinyl acetate (100 mL), hydrogen peroxide (60 mL, 27.5 wt. % solution in water) and 1-propanol (100 mL) were refluxed at 100°C for 3 days under nitrogen. 1-Propanol was then removed *in vacuo* and the resulting viscous oil was dissolved in dichloromethane. The solution was washed with water (3 x 100 mL) and dried over anhydrous magnesium sulphate. Dichloromethane was then removed under high vacuum and any remaining water removed by an azeotropic distillation using toluene.

The molecular number Mn was determined by GPC using methyl methacrylate standards to be about 1055. The yield was about 30%.

The polymer precursor was characterised by ¹H NMR, ¹³C NMR and ¹H-¹³C correlation NMR and as well as by COSY, IR and GPC.

Example 2: Preparation of Polymer Precursor I



This illustrates step (a) of the polymer precursor preparation process according to the present invention.

Vinyl acetate and ethanol were deoxygenated by a stream of nitrogen for at least 30 minutes immediately prior to use. A mixture of vinyl acetate (100 mL), hydrogen peroxide (60 mL, 27.5 wt. % solution in water) and ethanol (100 mL) were refluxed at 84°C for 8 days under nitrogen. Ethanol was then removed *in vacuo* and the resulting viscous oil was dissolved in dichloromethane. The solution was washed with water (3 x 100 mL) and dried over anhydrous magnesium sulphate. Dichloromethane was then removed under high vacuum and any remaining water removed by an azeotropic distillation using toluene.

The molecular number Mn was determined by GPC using methyl methacrylate standards to be about 1000. The number of OH equivalents determined twice by titration was 2.08 and 2.20. The yield was about 18%.

The polymer precursor was characterised by ^1H NMR, ^{13}C NMR and ^1H - ^{13}C correlation NMR and as well as by COSY, IR and GPC.

Example 3: Preparation of Polymer Precursor II

$\text{Br}(\text{Me})_2\text{CC}(\text{O})\text{O}(\text{CH}_2\text{CH}(\text{OAc}))_x(\text{CH}(\text{OAc})\text{CH}_2)_y\text{OC}(\text{O})\text{CMe}_2\text{Br}$.

5

This illustrates step (b) of the polymer precursor preparation process according to the present invention.

The polymer precursor I prepared in Example 2 (14.08 g, 15.3 mmol) was dissolved in anhydrous tetrahydrofuran (300 mL) with triethylamine (5.20 mL, 37.3 mmol) under nitrogen. 2-Bromoisobutyryl bromide (4.20 mL, 34.0 mmol) was added dropwise with vigorous stirring at 0°C and the reaction mixture stirred at room temperature overnight. The resulting precipitate was filtered off, the tetrahydrofuran removed *in vacuo* and the resulting viscous oil dissolved in dichloromethane. The solution was washed with saturated hydrogen carbonate (3 x 50 mL), dried over anhydrous magnesium sulphate and the dichloromethane removed under high vacuum to give a bright orange oil.

The polymer precursor was characterised by ^1H NMR (Figure 1(a)), ^{13}C pendants NMR (Figure 1(b)), COSY (Figure 1(c)) and ^1H - ^{13}C correlation NMR (Figure 1(d)), IR (Figure 2) and GPC (Figure 3). The compound prepared by the same method, but from a different batch was also characterised by DSC (Figure 4) (sample weight 1.000 mg).

TABLE 1 - Data for Figure 1(a) Example 3 (APJ 36)

NAME : Nov23-1998		EXPNO	: 30	PROCNO : 1
<u>F2 - Acquisition Parameters</u>				
5	Date	981123	Time	20.20
	INSTRUM	dpx300	RG	64
	PULPROG	zg30	DE	6.00 usec
	TD	32768	D1	1.00000000 sec
	SOLVENT	CDCl3	SF01	300.1318534 MHz
10	NS	16	NUC1	1H
	SWH	6172.839 Hz		
	AQ	2.6542580 sec		
<u>F2 - Processing Parameters</u>				
	SI	32768	LB	-0.20 Hz
15	WDW	EM	GB	0
<u>1D NMR plot parameters</u>				
	PPMCM	0.25641 ppm/cm	HZCM	76.95641 Hz/cm

TABLE 2 - Data for Figure 1(b) Example 3 (APJ 36)

NAME : Nov23-1998		EXPNO : 34		PROCNO : 1	
<u>F2 - Acquisition Parameters</u>					
5	Date	981123	Time	20.49	
	INSTRUM	dpx300	p2	50000000.00 usec	
	PULPROG	pendant	p4	50000000.00 usec	
	TD	65536	CNST2	500000.0000000	
	SOLVENT	CDCl3	d4	50000000.00000000 sec	
10	NS	128	d15	50000000.00000000 sec	
	SWH	18832.393 Hz	D1	500000.00000000 sec	
	AQ	1.7400308 sec	NUC2	1H	
	RG	4096	SF01	75.4763978 MHz	
	DE	6.00 usec	NUC1	13C	
15					
<u>F2 - Processing Parameters</u>					
	SI	32768	LB	2.00 Hz	
	WDW	EM	GB	0	
<u>1D NMR plot parameters</u>					
20	PPMCM	5.64103 ppm/cm	HZCM	425.71533 Hz/cm	

TABLE 3 - Data for Figure 1(c) Example 3 (APJ 36)

NAME : Nov23-1998 EXPNO : 31 PROCNO : 1			
<u>F2 - Acquisition Parameters</u>			
5	Date	981123	Time 20.21
	INSTRUM	dpx300	d0 0.00000300 sec
	PULPROG	cosygs	d13 0.00000300 sec
	TD	2048	D1 0.79888493 sec
	SOLVENT	CDCI3	SF01 300.1311641 MHz
10	NS	1	NUC1 1H
	SWH	2332.090 Hz	RG 32
	AQ	0.4391412 sec	DE 6.00 usec
<u>F1 - Acquisition Parameters</u>			
	NDO	1	FIDRES 9.109725 Hz
15	TD	256	SW 7.770 ppm
	SF01	300.1312 MHz	
<u>F2 - Processing Parameters</u>			
	SI	1024	LB 0.00 Hz
	WDW	SINE	GB 0
20	<u>F1-Processing Parameters</u>		
	SI	1024	SSB 0
	MC2	QF	LB 0.00 Hz
	SF	300.1300089 MHz	GB 0
	WDW	SINE	
25	<u>2D NMR plot parameters</u>		
	F2PPMCM	0.38851 ppm/cm	F2HZCM 116.60403 Hz/cm
	F1PPMCM	0.38851 ppm/cm	F1HZCM 116.60403 Hz/cm

TABLE 4 - Data for Figure 1(d) Example 3 (APJ 36)

	NAME : Nov23-1998		EXPNO : 33		PROCNO : 1	
	<u>F2 - Acquisition Parameters</u>					
5	Date	981123	Time	20.30		
	INSTRUM	dpx300	p2	50000000.00 sec		
	PULPROG	inv4gs	d0	50000000.00000000 sec		
	TD	1024	CNST2	500000.00000000		
	SOLVENT	CDCI3	d2	50000000.00000000 sec		
10	NS	2	d12	50000000.00000000 sec		
	SWH	2495.010 Hz	d13	50000000.00000000 sec		
	AQ	0.2052596 sec	d20	50000000.00000000 sec		
	RG	13004	D1	500000.00000000 sec		
	DE	6.00 usec	SF01	300.1307992 MHz		
15	NUC1	1H	NUC2	13C		
	<u>F1 - Acquisition Parameters</u>					
	NDO	2	FIDRES	130.643814 Hz		
	TD	128	SW	221.562 ppm		
	SF01	75.47522 MHz				
20	<u>F2 - Processing Parameters</u>					
	SI	2048	LB	0.00 Hz		
	WDW	QSINE		GB	0	
	<u>F1-Processing Parameters</u>					
	SI	1024	SSB	5		
25	MC2	QF	LB	0.00 Hz		
	SF	75.4677190 MHz	GB	0		
	WDW	QSINE				
	<u>2D NMR plot parameters</u>					
	F2PPMCM	0.26816 ppm/cm	F2HZCM	80.48398 Hz/cm		
30	F1PPMCM	11.07808 ppm/cm	F1HZCM	836.03729 Hz/cm		

TABLE 5 - GPC ANALYSIS Figure 3 Example 3

	Sample name : apj182	Raw date filename : 24111.003
	<u>Conditions :</u>	
5	Solvent : THF	Temperature : room temp.
	Column set : one mixed E column and guard	Flow rate : 1.00 mL/min
	Detector : RI	
	<u>Data Processing :</u>	
	Method : 1 Calibration using : Narrow standards	
10	Calibration limits : 5.75 to 11.22 Mins	
	Curve used : 3 rd order polynomial	Coefficients : $\text{Log}(M) = A + BT + CT^2 + DT^3$
	A=11.557600, B = 1.747136, C = 0.119394, D = 0.003592	
	Last calibrated : Oct 20 14:17:10 1998	
	Flow rate marker : found at 11.23 in standards at 11.15 Mins.	
15	Broad peak start : 6.48 end : 10.27 Mins.	
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.697	0.697
	<u>Molecular weight results :</u>	
20	Mp = 1745	Mn = 1128 Mw = 2156
	Mz = 3823	Mz+1 = 5989 Mv = 1963
	Polydispersity = 1.911	Peak area = 39878

Example 4 : Preparation of Polymer Precursor III

$\text{HOCH}_2\text{CH}_2\text{NHC(O)-C(Me)}_2(\text{CH}_2\text{CH(OAc)})_x(\text{CH(OAc)CH}_2)_y\text{C(Me)}_2\text{C(O)-NH-CH}_2\text{-CH}_2\text{-OH}$

5 This illustrates step (a) of the polymer precursor preparation process according to the present invention.

Vinyl acetate and 1-propanol were deoxygenated by a stream of nitrogen for at least 30 minutes immediately prior to use. To a mixture of deoxygenated vinyl acetate (107.7 mL) and 1-propanol (200 mL) was added to the Azo initiator (Wako, VA-086) (2.8835g) having the formula :

10 $\text{HOCH}_2\text{CH}_2\text{NH C(O)C(Me)}_2\text{N=NC(Me)}_2\text{C(O)NH-CH}_2\text{CH}_2\text{OH.}$

The solution was refluxed under a nitrogen atmosphere overnight at 104°C. The initiator dissolved on warming. A biphasic solution was obtained on cooling the reaction mixture. The solvent was removed *in vacuo* and any remaining water removed by an azeotropic distillation using toluene.

15 From GPC, $M_n = 8930$ (using methyl methacrylate standards). Yield was 85 %.

The polymer precursor was characterised by ^1H NMR (Figure 5(a)), ^{13}C pendant NMR (Figure 5(b)), COSY (Figure 5(c)) and ^1H - ^{13}C correlation NMR (Figure 5(d)) as well as by IR (Figure 6) and GPC (Figure 7).

20

TABLE 6 - Data for Figure 5(a) Example 4 (APJ 14)

NAME : Feb08-1999		EXPNO	: 23	PROCNO : 1
<u>F2 - Acquisition Parameters</u>				
5	Date	990208	Time	23.27
	INSTRUM	dpx300	RG	128
	PULPROG	zg30	DE	6.00 usec
	TD	32768	D1	1.00000000 sec
	SOLVENT	CDCI3	SF01	300.1318534 MHz
10	NS	16	NUC1	1H
	SWH	6172.839 Hz		
	AQ	2.6542580 sec		
<u>F2 - Processing Parameters</u>				
	SI	32768	LB	-0.20 Hz
15	WDW	EM	GB	0
<u>1D NMR plot parameters</u>				
	PPMCM	0.25641 ppm/cm	HZCM	76.95641 Hz/cm

TABLE 7 - Data for Figure 5(b) Example 4 (APJ 14)

	NAME : Feb08-1999		EXPNO : 22		PROCNO : 1	
	<u>F2 - Acquisition Parameters</u>					
5	Date	990208	Time	23.25		
	INSTRUM	dpx300	p2	50000000.00 usec		
	PULPROG	pendant	p4	50000000.00 usec		
	TD	65536	CNST2	500000.0000000		
	SOLVENT	CDCl3	d4	50000000.00000000 sec		
10	NS	512	d15	50000000.00000000 sec		
	SWH	18832.393 Hz	D1	500000.00000000 sec		
	AQ	1.7400308 sec	NUC2	1H		
	RG	11585.2	SF01	75.4763978 MHz		
	DE	6.00 usec	NUC1	13C		
15						
	<u>F2 - Processing Parameters</u>					
	SI	32768	LB	2.00 Hz		
	WDW	EM	GB	0		
	<u>1D NMR plot parameters</u>					
20	PPMCM	5.64103 ppm/cm	HZCM	425.71533 Hz/cm		

TABLE 8 - Data for Figure 5(c) Example 4 (APJ 14)

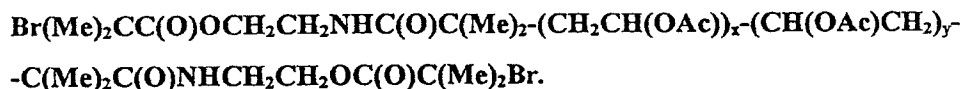
	NAME : Feb08-1999		EXPNO : 21	PROCNO : 1
	<u>F2 - Acquisition Parameters</u>			
5	Date	990208	Time	22.46
	INSTRUM	dpx300	d0	0.00000300 sec
	PULPROG	cosygs	d13	0.00000300 sec
	TD	2048	D1	0.8234608 sec
	SOLVENT	CDCI3	SF01	300.1311471 MHz
10	NS	1	NUC1	1H
	SWH	2480.159 Hz	RG	80.6
	AQ	0.4129268 sec	DE	6.00 usec
	<u>F1 - Acquisition Parameters</u>			
	NDO	1	FIDRES	9.688120 Hz
15	TD	256	SW	8.264 ppm
	SF01	300.1311 MHz		
	<u>F2 - Processing Parameters</u>			
	SI	1024	LB	0.00 Hz
	WDW	SINE	GB	0
20	<u>F1-Processing Parameters</u>			
	SI	1024	SSB	0
	MC2	QF	LB	0.00 Hz
	SF	300.1300236 MHz	GB	0
	WDW	SINE		
25	<u>2D NMR plot parameters</u>			
	F2PPMCM	0.41318 ppm/cm	F2HZCM	124.00748 Hz/cm
	F1PPMCM	0.41318 ppm/cm	F1HZCM	124.00748 Hz/cm

TABLE 9 - Data for Figure 5(d) Example 4 (APJ 14)

NAME : Feb08-1999 EXPNO : 24 PROCNO : 1			
<u>F2 - Acquisition Parameters</u>			
5	Date	990208	Time 23.28
	INSTRUM	dpx300	p2 50000000.00 sec
	PULPROG	inv4gs	d0 50000000.00000000 sec
	TD	1024	CNST2 500000.00000000
	SOLVENT	CDCI3	d2 50000000.00000000 sec
10	NS	2	d12 50000000.00000000 sec
	SWH	2637.131 Hz	d13 50000000.00000000 sec
	AQ	0.1942004 sec	d20 50000000.00000000 sec
	RG	13004	D1 500000.00000000 sec
	DE	6.00 usec	SF01 300.1310966 MHz
15	NUC1	1H	NUC2 13C
<u>F1 - Acquisition Parameters</u>			
	NDO	2	FIDRES 130.643814 Hz
	TD	128	SW 221.562 ppm
	SF01	75.47522 MHz	
20	<u>F2 - Processing Parameters</u>		
	SI	2048	LB 0.00 Hz
	WDW	QSINE	GB 0
<u>F1-Processing Parameters</u>			
	SI	1024	SSB 5
25	MC2	QF	LB 0.00 Hz
	SF	75.4677190 MHz	GB 0
	WDW	QSINE	
<u>2D NMR plot parameters</u>			
	F2PPMCM	0.28344 ppm/cm	F2HZCM 85.06844 Hz/cm
30	F1PPMCM	11.07808 ppm/cm	F1HZCM 836.03729 Hz/cm

TABLE 10 - GPC ANALYSIS Figure 7 Example 4

	Sample name : apj	Raw date filename : 15072.002
	<u>Conditions :</u>	
5	Solvent : THF	Temperature : room temp.
	Column set : one guard column and 2 mixed D	Flow rate : 1.00 mL/min
	Detector : DRI	
	<u>Data Processing :</u>	
	Method : 2	Calibration using : Narrow standards
10	Calibration limits : 9.83 to 17.98 Mins	
	Curve used : 3 rd order polynomial	Coefficients : Log(M) = A + BT + CT ² + DT ³
	A=18.699185, B = 2.346432, C = 0.135302, D = 0.003040	
	Last calibrated : Fri Jun 25 08:41:02 1999	
	Flow rate marker : found at 20.42 in standards at 20.37 Mins.	
15	Broad peak start : 11.22 end : 17.15 Mins.	
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.697	0.697
	<u>Molecular weight results :</u>	
20	Mp = 19056	Mn = 7501 Mw = 19315
	Mz = 36240	Mz+1 = 53447 Mv = 17185
	Polydispersity = 2.575	Peak area = 25182

Example 5 : Preparation of Polymer Precursor IV

- 5 This illustrates step (b) of the polymer precursor preparation process according to the present invention. The polymer precursor III prepared in Example 4 (38.93 g, 4.36 mmol) was dissolved in anhydrous tetrahydrofuran (300 mL) with triethylamine (1.46 mL, 10.46 mmol) under nitrogen. 2-Bromoisobutyryl bromide (1.29 mL, 10.5 mmol) was added dropwise with vigorous stirring at 0°C and the reaction mixture stirred
- 10 at room temperature overnight. The resulting precipitate was filtered off, the tetrahydrofuran removed *in vacuo* and the resulting viscous oil dissolved in dichloromethane. The solution was washed with saturated hydrogen carbonate (3 x 50 mL), dried over anhydrous magnesium sulphate and the dichloromethane removed under high vacuum to give a bright orange oil.
- 15 The polymer precursor was characterised by ¹H NMR (Figure 8(a)), ¹³C pendant NMR (Figure 8(b)), COSY (Figure 8(c)) and ¹H- ¹³C correlation NMR (Figure 8(d)) as well as by IR (Figure 9) and GPC (Figure 10).

TABLE 11 - Data for Figure 8(a) Example 5 (APJ 58)

	NAME : Mar17-1999		EXPNO	: 10	PROCNO : 1
	<u>F2 - Acquisition Parameters</u>				
5	Date	990317	Time	23.02	
	INSTRUM	dpx300	RG	32	
	PULPROG	zg30	DE	6.00 usec	
	TD	32768	D1	1.00000000 sec	
	SOLVENT	CDCl3	SF01	300.1318534 MHz	
10	NS	16	NUC1	1H	
	SWH	6172.839 Hz			
	AQ	2.6542580 sec			
	<u>F2 - Processing Parameters</u>				
	SI	32768	LB	-0.20 Hz	
15	WDW	EM	GB	0	
	<u>1D NMR plot parameters</u>				
	PPMCM	0.25641 ppm/cm	HZCM	76.95641 Hz/cm	

TABLE 12 - Data for Figure 8(b) Example 5 (APJ 58)

	NAME : Mar17-1999		EXPNO : 12		PROCNO : 1	
	<u>F2 - Acquisition Parameters</u>					
5	Date	990317	Time	23.42		
	INSTRUM	dpx300	p2	50000000.00 usec		
	PULPROG	pendant	p4	50000000.00 usec		
	TD	65536	CNST2	500000.0000000		
	SOLVENT	CDCl3	d4	50000000.00000000 sec		
10	NS	512	d15	50000000.00000000 sec		
	SWH	18832.393 Hz	D1	500000.00000000 sec		
	AQ	1.7400308 sec	NUC2	1H		
	RG	7298.2	SF01	75.4763978 MHz		
	DE	6.00 usec	NUC1	13C		
15						
	<u>F2 - Processing Parameters</u>					
	SI	32768	LB	2.00 Hz		
	WDW	EM	GB	0		
	<u>1D NMR plot parameters</u>					
20	PPMCM	5.64103 ppm/cm	HZCM	425.71533 Hz/cm		

TABLE 13 - Data for Figure 8(c) Example 5 (APJ 58)

	NAME : Mar17-1999		EXPNO : 11	PROCNO : 1
	<u>F2 - Acquisition Parameters</u>			
5	Date	990317	Time	23.03
	INSTRUM	dpx300	d0	0.00000300 sec
	PULPROG	cosygs	d13	0.00000300 sec
	TD	2048	D1	0.79683691 sec
	SOLVENT	CDCI3	SF01	300.1311718 MHz
10	NS	1	NUC1	1H
	SWH	2332.090 Hz	RG	16
	AQ	0.4391412 sec	DE	6.00 usec
	<u>F1 - Acquisition Parameters</u>			
	NDO	1	FIDRES	9.109725 Hz
15	TD	256	SW	7.770 ppm
	SF01	300.1312 MHz		
	<u>F2 - Processing Parameters</u>			
	SI	1024	LB	0.00 Hz
	WDW	SINE	GB	0
20	<u>F1-Processing Parameters</u>			
	SI	1024	SSB	0
	MC2	QF	LB	0.00 Hz
	SF	300.1299922 MHz	GB	0
	WDW	SINE		
25	<u>2D NMR plot parameters</u>			
	F2PPMCM	0.38851 ppm/cm	F2HZCM	116.60403 Hz/cm
	F1PPMCM	0.38851 ppm/cm	F1HZCM	116.60403 Hz/cm

TABLE 14 - Data for Figure 8(d) Example 5 (APJ 58)

NAME : Mar17-1999 EXPNO : 14 PROCNO : 1			
<u>F2 - Acquisition Parameters</u>			
5	Date	990317	Time 23.46
	INSTRUM	dpx300	p2 50000000.00 sec
	PULPROG	inv4gs	d0 50000000.00000000 sec
	TD	1024	CNST2 500000.00000000
	SOLVENT	CDCl3	d2 50000000.00000000 sec
10	NS	2	d12 50000000.00000000 sec
	SWH	2653.928 Hz	d13 50000000.00000000 sec
	AQ	0.1929716 sec	d20 50000000.00000000 sec
	RG	6502	D1 500000.00000000 sec
	DE	6.00 usec	SF01 300.1310520 MHz
15	NUC1	1H	NUC2 13C
<u>F1 - Acquisition Parameters</u>			
	NDO	2	FIDRES 130.643814 Hz
	TD	128	SW 221.562 ppm
	SF01	75.47522 MHz	
20	<u>F2 - Processing Parameters</u>		
	SI	2048	LB 0.00 Hz
	WDW	QSINE	GB 0
<u>F1-Processing Parameters</u>			
	SI	1024	SSB 5
25	MC2	QF	LB 0.00 Hz
	SF	75.4677190 MHz	GB 0
	WDW	QSINE	
<u>2D NMR plot parameters</u>			
	F2PPMCM	0.28524 ppm/cm	F2HZCM 85.61028 Hz/cm
30	F1PPMCM	11.07808 ppm/cm	F1HZCM 836.03729 Hz/cm

TABLE 15 - GPC ANALYSIS Figure 10 Example 5

	Sample name : aj1114	Raw date filename : 25062.002
	<u>Conditions :</u>	
5	Solvent : THF	Temperature : room temp.
	Column set : one guard column and 2 mixed D	Flow rate : 1.00 mL/min
	Detector : DRI	
	<u>Data Processing :</u>	
	Method : 2	Calibration using : Narrow standards
10	Calibration limits : 9.80 to 17.93 Mins	
	Curve used : 3 rd order polynomial	Coefficients : $\text{Log}(M) = A + BT + CT^2 + DT^3$
	A=18.699185, B = 2.346432, C = 0.135302, D = 0.003040	
	Last calibrated : Fri Jun 25 08:41:02 1999	
	Flow rate marker : found at 20.35 in standards at 20.37 Mins.	
15	Broad peak start : 11.15 end : 16.97 Mins.	
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.697	0.697
	<u>Molecular weight results :</u>	
20	Mp = 19699	Mn = 9183 Mw = 20468
	Mz = 35738	Mz+1 = 51313 Mv = 18502
	Polydispersity = 2.229	Peak area = 25866

Atom transfer polymerisation of vinyl monomers using α, ω difunctional polymer**precursors****Preparation of organodiimine ligands****Preparation of N-propyl-pyridinal methanimine**

To a solution of pyridine-2-carboxaldehyde (1.78 mL, 1.87×10^{-2} mol) and diethyl ether (30 mL) was added n-propylamine (1.55 mL, 1.88×10^{-2} mol). The reaction mixture was stirred for 10 minutes at room temperature prior to addition of anhydrous magnesium sulphate and stirring for a further 30 minutes. The magnesium

sulphate was removed by filtration, and volatiles were removed under reduced pressure to give the product in quantitative yield as a pale yellow oil.

¹H NMR (CDCl₃, 373 K, 400.13 MHz): d = 8.51 (d, *J* = 3.5 Hz, 1H) 8.26 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 4.6 Hz, 1H), 3.52 (t, *J* = 7.6 Hz, 2H), 1.63 (sext, *J* = 7.3 Hz, 2H), 0.84 (t, *J* = 7.5 Hz, 3H). ¹³C (CDCl₃, 373K, 100.61 MHz) : d = 161.51, 154.44, 149.18, 136.28, 124.37, 120.97, 63.08, 23.65, 11.65 ppm. IR (NaCl, film), 3053-2830, 1648, 1587, 1566, 772, 742 cm⁻¹. Bp = 218°C.

Preparation of N-octyl-pyridinal methanimine.

To a solution of pyridine-2-carboxaldehyde (19 mL, 0.20 mol) and diethyl ether (150 mL) in a 250 mL round-bottomed flask was added octylamine (33.9 mL, 0.20 mol). The reaction mixture was stirred for 1 hour prior to addition of anhydrous magnesium sulphate (25.2 g) and stirring for a further 2 hours. The magnesium sulphate was removed by filtration and was washed with diethyl ether. The ether was subsequently removed by rotary evaporation to give a dark yellow viscous liquid. The liquid was fractionally distilled at 96 °C at 0.04 torr to give a pale yellow liquid. Yield = 40.5 g (90.5%). ¹H NMR (CDCl₃, 298 K, 250.13 MHz) d = 8.60 (d, *J* = 4.9 Hz, 1H) 8.33 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 6.2 Hz, 1H), 3.63 (t, *J* = 7.0 Hz, 2H), 1.68 (m, *J* = 7.0 Hz, 2H), 1.26 (m, *J* = 7.3 Hz, 10H), 0.82 (t, *J* = 7.0 Hz, 3H). ¹³C (CDCl₃, 298K, 100.16 MHz) : 161.1, 154.5, 148.8, 135.7, 123.9, 120.5, 61.1, 31.5, 30.4, 29.1, 28.9, 27.0, 22.3, 13.7. Anal. Calc. for C₁₄H₂₂N₂ : C = 77.01, H = 10.16, N = 12.82. Found C = 77.15, H = 10.25, N = 12.85.

General procedure for atom transfer polymerisation.

Monomers were passed down a basic alumina column (Aldrich, Brockmann I grade) immediately prior to use, degassed by a stream of nitrogen for at least 30 minutes and freeze-pump-thawed (three times). Solvents were deoxygenated by a stream of nitrogen for at least 30 minutes prior to use. Cu(I)Br was purified according to a published procedure (Keller, R.N. and Weycoff, M.D. Inorg. Synth. 1947, 2,1.). All atom transfer polymerisation experiments carried out at 90°C except for those involving styrene which were heated to 110°C. A slight excess of ligand (10%) is added to the reaction mixture.

The atom transfer polymerisation experiments have been carried out using slightly varying methods.

Example 6 : Polymerisation of methyl methacrylate with polymer precursor II.

- Polymer precursor, initiator, prepared in Example 3 (1.48 g, 1.0 mmol) and a magnetic follower were placed in a Schlenk tube. Toluene (10.70 mL), N-octyl-pyridinal methanimine (0.96 g, 4.2 mmol) prepared as hereinbefore described and monomer
- 5 (methyl methacrylate) (5.34 mL) were added. The solution was deoxygenated via three freeze-pump-thaw cycles and added to Cu(I)Br (0.286g, 2.0 mmol). Reaction mixture subsequently heated to 90°C or 110°C depending on the monomer used. Samples were removed by syringe periodically (every 30 minutes) for analysis (GPC and gravimetrically). All molecular weight data was recorded on un-precipitated polymer.
- 10 The final polymer solution was passed down a basic alumina column and precipitated into n-pentane.

This illustrates preparation of a block polymer according to the present invention using a molar ratio of ratio of monomer : polymer precursor : metal : ligand of 100:1:2:4 in 66% toluene solution. The reaction was terminated at about 96% conversion.

- 15 The molecular number Mn was determined by GPC using methyl methacrylate standards to be about 27340 (Figure 11).

TABLE 16 - GPC ANALYSIS Figure 11 Example 6(a)

	Sample name : aj1789		Raw date filename : 02112.017	
	<u>Conditions :</u>			
5	Solvent :	THF with toluene	Temperature : room temp.	
	Column set :	one guard column and 2 mixed D	Flow rate : 1.00 mL/min	
	Detector :	DRI/UV		
	<u>Data Processing :</u>			
	Method :	2 Calibration using : Narrow standards		
10	Calibration limits :	10.00 to 20.65 Mins		
	Curve used :	3 rd order polynomial	Coefficients : Log(M) = A + BT + CT ² + DT ³	
		A=11.819727, B = 0.759678, C = 0.016374, D = 0.000144		
	Last calibrated :	Wed Oct 21 10:54:26 1998		
	Flow rate marker :	found at 20.67 in standards at 20.38 Mins.		
15	Broad peak start :	11.08	end : 15.08 Mins.	
		Standards	Sample	
	K :	10.4000*10e-5	10.4000* 10e-5	
	alpha :	0.697	0.697	
	<u>Molecular weight results :</u>			
20	Mp = 35898	Mn = 27342	Mw = 41579	
	Mz = 58673	Mz+1 = 76178	Mv = 39238	
	Polydispersity = 1.521	Peak area = 5112		

The polymer precursor was also characterised by DSC (Figure 12) (3.000 mg sample weight Total Mn - 33000 heat from -50.00°C to 140.00°C at 20.00°C/min).

This example (Example 6(a)) was repeated using different monomers and different molar ratios of reagents as follows :

Example 6 (b) : The monomer used was methyl methacrylate.

Molar ratio of monomer : polymer precursor : metal : ligand = 50 : 1 : 2 : 4.

Product Mn = 14490 using poly(methyl methacrylate) standard for GPC (Figure 13).

TABLE 17 - GPC ANALYSIS Figure 13 Example 6(b)

	Sample name : aj1569	Raw date filename : 02112.026
	<u>Conditions :</u>	
5	Solvent : THF with toluene	Temperature : room temp.
	Column set : one guard column and 2 mixed D	Flow rate : 1.00 mL/min
	Detector : DRI/UV	
	<u>Data Processing :</u>	
	Method : 2	Calibration using : Narrow standards
10	Calibration limits : 9.97 to 20.60 Mins	
	Curve used : 3 rd order polynomial	Coefficients : Log(M) = A + BT + CT ² + DT ³
	A=11.819727, B = 0.759678, C = 0.016374, D = 0.000144	
	Last calibrated : Wed Oct 21 10:54:26 1998	
	Flow rate marker : found at 20.62 in standards at 20.38 Mins.	
15	Broad peak start : 11.58	end : 15.78 Mins.
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.697	0.697
	<u>Molecular weight results :</u>	
20	Mp = 19651	Mn = 14489 Mw = 21615
	Mz = 30835	Mz+1 = 41305 Mv = 20405
	Polydispersity = 1.492	Peak area = 6773

The polymer precursor was also characterised by DSC (Figure 14) (sample weight 8.100 mg , Total Mn - 17000, heat from -60.00°C to 140.00°C at 20.00°C/min.) and by ¹H NMR in CDCl₃ (Figure 15).

Example 6 (c) : The monomer used was styrene.

Molar ratio of monomer : polymer precursor : metal : ligand = 100 : 1 : 2 : 4.

Product Mn = 16440 using poly(styrene) standard for GPC (Figure 16).

30

TABLE 18 - GPC ANALYSIS Figure 16 Example 6(c)

	Sample name : apj1669	Raw date filename : 29102.009
	<u>Conditions :</u>	
5	Solvent : THF with toluene	Temperature : room temp.
	Column set : one guard column and 2 mixed D	Flow rate : 1.00 mL/min
	Detector : DRI/UV	
	<u>Data Processing :</u>	
	Method : 21 Calibration using : Narrow standards	
10	Calibration limits : 9.58 to 20.67 Mins	
	Curve used : 3 rd order polynomial	Coefficients : Log(M) = A + BT + CT ² + DT ³
	A=13.147278, B = 1.020344, C = 0.032583, D = 0.000469	
	Last calibrated : Wed Oct 21 11:04:12 1998	
	Flow rate marker : found at 20.67 in standards at 20.40 Mins.	
15	Broad peak start : 11.52 end : 15.85 Mins.	
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.700	0.700
	<u>Molecular weight results :</u>	
20	Mp = 24042	Mn = 16442 Mw = 24927
	Mz = 35106	Mz+1 = 45798 Mv = 23556
	Polydispersity = 1.516	Peak area = 7693

25 The polymer precursor was also characterised by DSC (Figure 17) (1.00 mg sample weight, total Mn - 17000, heat from -50.00°C to 140.00°C at 20.00°C/min) and by ¹H NMR CDCl₃ (Figure 18).

Example 6 (d) : The monomer used was n-butyl methacrylate.

Molar ratio of monomer : polymer precursor : metal : ligand = 100 : 1 : 2 : 4.

Product Mn = 13190 using poly(methyl methacrylate) standard for GPC (Figure 19).

30

TABLE 19 - GPC ANALYSIS Figure 19 Example 6(d)

	Sample name : apj188 11		Raw date filename : 01122.038	
	<u>Conditions :</u>			
5	Solvent :	THF with toluene	Temperature : room temp.	
	Column set :	one guard column and 2 mixed D	Flow rate : 1.00 mL/min	
	Detector :	DRI/UV		
	<u>Data Processing :</u>			
	Method :	2 Calibration using : Narrow standards		
10	Calibration limits :	9.88 to 20.42 Mins		
	Curve used :	3 rd order polynomial	Coefficients : Log(M) = A + BT + CT ² + DT ³	
	A=11.821880, B = 0.759705, C = 0.016359, D = 0.000144			
	Last calibrated : Sun Nov 15 11:08:30 1998			
	Flow rate marker : found at 20.43 in standards at 20.38 Mins.			
15	Broad peak start : 11.23 end : 16.10 Mins.			
		Standards	Sample	
	K :	10.4000*10e-5	10.4000* 10e-5	
	alpha :	0.697	0.697	
	<u>Molecular weight results :</u>			
20	Mp = 17626	Mn = 13190	Mw = 21880	
	Mz = 33488	Mz+1 = 47717	Mv = 20421	
	Polydispersity = 1.659		Peak area = 2996	

The polymer precursor was also characterised by ¹H NMR in CDCl₃ (Figure 20).

25 Example 6 (e) : The monomer used was n-butyl methacrylate.

Molar ratio of monomer : polymer precursor : metal : ligand = 50 : 1 : 2 : 4.

Product Mn = 8490 using poly(methyl methacrylate) standard for GPC (Figure 21).

TABLE 20 - GPC ANALYSIS Figure 21 Example 6(e)

	Sample name : apj188 30		Raw date filename : 01122.048	
	<u>Conditions :</u>			
5	Solvent :	THF with toluene	Temperature : room temp.	
	Column set :	one guard column and 2 mixed D	Flow rate : 1.00 mL/min	
	Detector :	DRI/UV		
	<u>Data Processing :</u>			
	Method :	2	Calibration using : Narrow standards	
10	Calibration limits :	9.88 to 20.42 Mins		
	Curve used :	3 rd order polynomial	Coefficients : Log(M) = A + BT + CT ² + DT ³	
		A=11.821880, B = 0.759705, C = 0.016359, D = 0.000144		
	Last calibrated :	Sun Nov 15 11:08:30 1998		
	Flow rate marker :	found at 20.42 in standards at 20.38 Mins.		
15	Broad peak start :	11.83	end : 16.55 Mins.	
		Standards	Sample	
	K :	10.4000*10e-5	10.4000* 10e-5	
	alpha :	0.697	0.697	
	<u>Molecular weight results :</u>			
20	Mp =	12694	Mn = 8486	Mw = 13647
	Mz =	20030	Mz+1 = 27335	Mv = 12805
	Polydispersity =	1.608	Peak area = 6699	

The polymer precursor was also characterised by DSC (Figure 22) (sample weight 3.200 mg, heat from -50.00°C to 120.00°C at 20.00°C/min) and by ¹H NMR in CDCl₃ (Figure 23).

Example 7: Polymerisation of styrene with polymer precursor IV.

Polymer precursor IV prepared in Example 5 (1.1044 g, 0.4 mmol), Cu(I)Br (0.1139 g, 0.8 mmol) and a magnetic follower were placed in a Schlenk tube. Deoxygenated toluene(4.40 mL) and N-propyl-2-pyridinal methanimine (0.26 g, 1.76 mmol) prepared as hereinbeforedescribed were added and the solution heated to 110°C.

Deoxygenated inhibitor free styrene (4.40 mL) was then added ($t = 0$). Samples were removed periodically for analysis, via syringe. All molecular weight data recorded on un-precipitated polymer. The final polymer solution was passed down a basic alumina column and precipitated into n-pentane.

- 5 This illustrates preparation of a block polymer according to the present invention using a molar ratio of monomer : polymer precursor : metal : ligand of 100 : 1 : 2 : 4 in 50% to toluene solution.

10

15

Claims :

1. A process for the preparation of a block polymer which process comprises a transition metal mediated, atom transfer polymerisation of an ethylenically unsaturated monomer with an α, ω di-functional polymer precursor having repeating units derived from an ethylenically unsaturated carboxylate.
- 5 2. A process as claimed in claim 1 wherein the ethylenically unsaturated carboxylate is vinyl acetate.
3. A process as claimed in claim 1 wherein the ethylenically unsaturated monomer is selected from the group consisting of styrene, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, acrylic acid, unsubstituted acrylate and methacrylate.
- 10 4. A process as claimed in claim 2 wherein the ethylenically unsaturated monomer is selected from the group consisting of styrene, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, acrylic acid, unsubstituted acrylate and methacrylate.
5. An α, ω di-functional polymer precursor having a molecular weight in the range from 500 to 50000 and being represented by the formula :

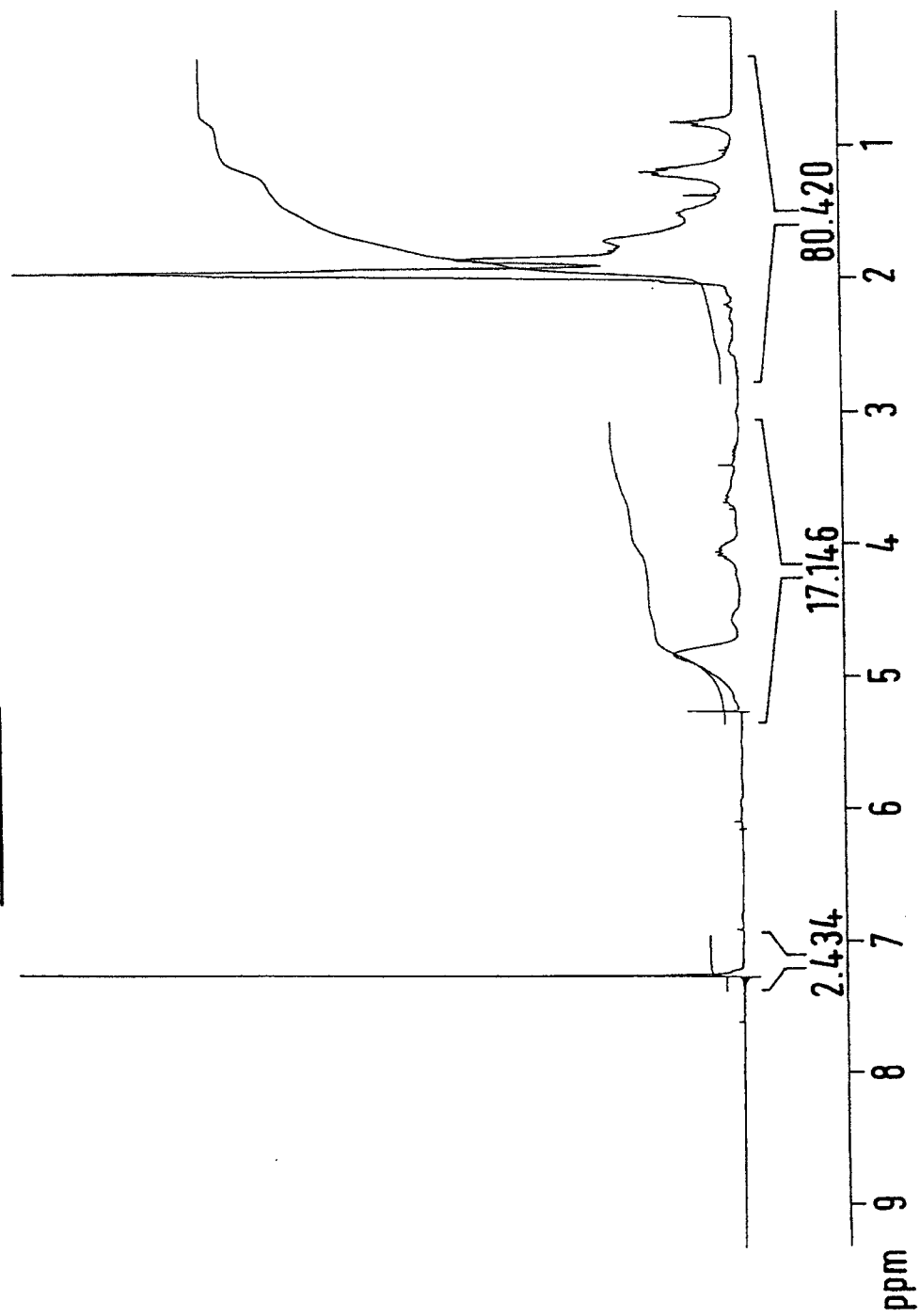
15
$$X-[-CH_2-CY(OR)-]_x-[-CY'(OR)-CH_2-]_y-X'$$
 wherein x and y are integers independently greater than 1; Y and Y' are independently H or $-CH_3$; R represents a hydrocarbyl group; and X and X' independently represent substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.
- 20 6. A polymer precursor as claimed in claim 5 wherein R is selected from the group consisting of $CH_3C(O)-$, $Y''-C(O)-$, $PhC(O)-$, $Ph-$, $PhCH_2-$,

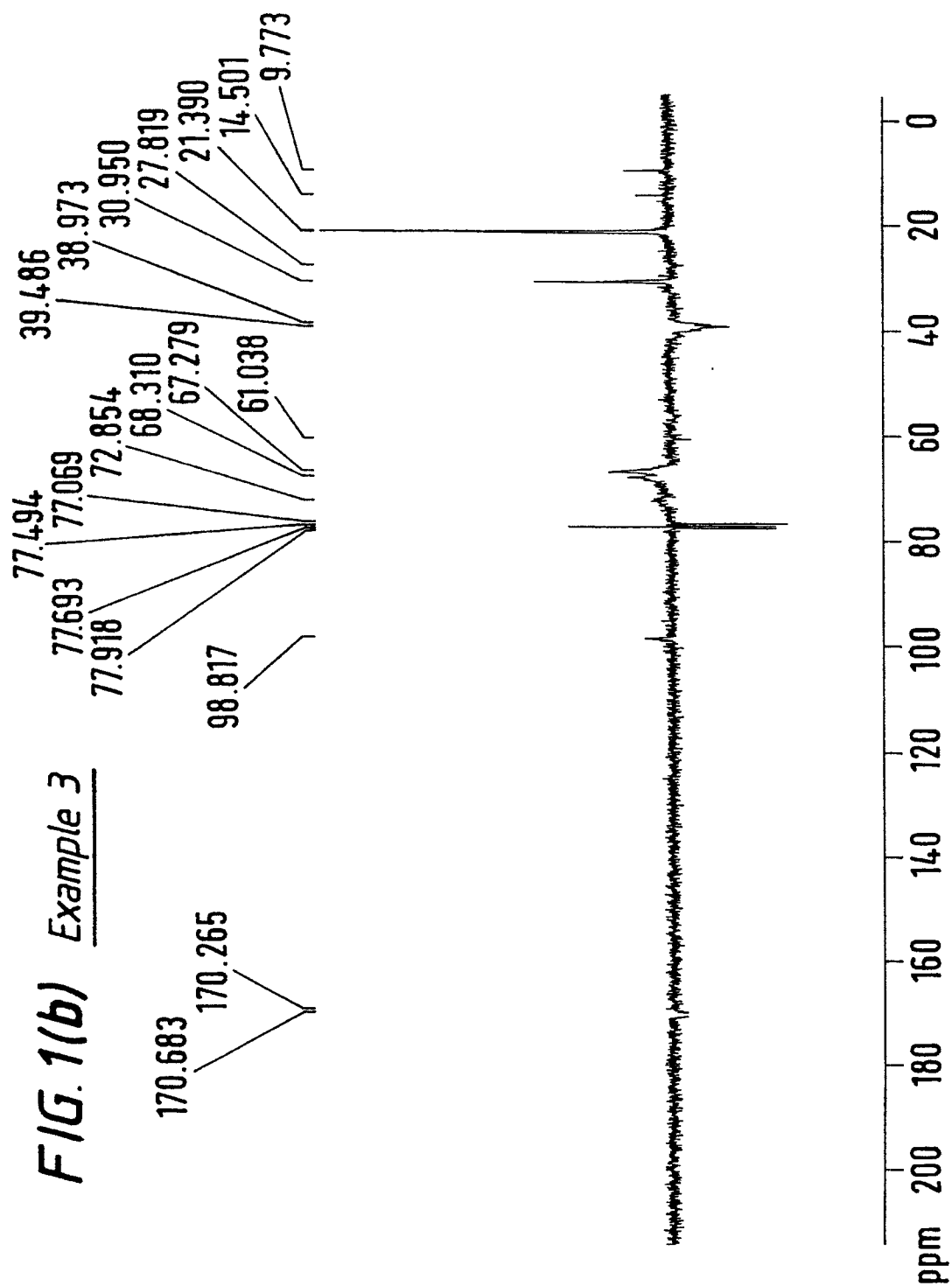
- CH₃-(CH₂-CH₂-CH₂-CH₂)_zC(O)-, CH₃-(CH₂-CH=CH-CH₂)_zC(O)- and substituted phenyl; wherein Y" is an n-alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z" is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent selected from the group consisting of NO₂, OMe, CN, NMe₂, OH, Cl, Br, and F.
- 5 7. A polymer precursor as claimed in claim 5 wherein R is CH₃C(O)-.
8. A process for the production of an α, ω di-functional polymer precursor which process comprises the steps of :
- (a) reacting an ethylenically unsaturated carboxylate with a radical initiator having a substitutable functional group; and
- 10 (b) substituting the functional groups on the product of step (a) with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.
9. A process as claimed in claim 8 wherein the ethylenically unsaturated carboxylate is vinyl acetate.
- 15 10. A polymer precursor having a molecular weight in the range from 500 to 50000, preferably from 1000 to 20000 and being represented by the formula :
- $$\text{HO}[-\text{CH}_2-\text{CY}(\text{OR}')-]_{x'}[-\text{CY}'(\text{OR}')-\text{CH}_2-]_{y'}\text{OH}$$
- wherein x' and y' are integers independently greater than 1; Y and Y' are independently H or -CH₃; and R' represents a hydrocarbyl group.
- 20 11. A polymer precursor as claimed in claim 10 wherein R' is selected from the group consisting of CH₃C(O)-, Y"-C(O)-, PhC(O)-, Ph-, PhCH₂-, CH₃-(CH₂-CH₂-CH₂-CH₂)_zC(O)-, CH₃-(CH₂-CH=CH-CH₂)_zC(O)- and substituted phenyl; wherein Y" is an n-alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z" is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent selected from the group consisting of NO₂, OMe, CN, NMe₂, OH, Cl, Br, and F.
- 25 12. A polymer precursor as claimed in claim 10 wherein R' is CH₃C(O)-.
13. A block polymer comprising alternating repeating units of -[A]- and -[B]- in which -A- represents a polymer block having a molecular weight in the range from 500 to 50000 and being represented by the formula :
- 30 -[CH₂-CY(OR'')-]_{x''}[-CY'(OR'')-CH₂-]_{y''}-

- wherein x'' and y'' are integers independently greater than 1; Y and Y' are independently H or $-\text{CH}_3$ and R'' represents a hydrocarbonyl group and -B- represents at least one polymer repeating unit selected from the group consisting of acrylic, substituted acrylic, methacrylic, substituted methacrylic, acrylonitrile, methacrylonitrile, acylamide, methacrylamide and styrenic polymer units.
14. A block polymer as claimed in claim 13 wherein R'' is selected from the group consisting of $\text{CH}_3\text{C}(\text{O})-$, $\text{Y}''-\text{C}(\text{O})-$, $\text{PhC}(\text{O})-$, Ph-, PhCH_2- , $\text{CH}_3-(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-)_{z'}\text{C}(\text{O})-$, $\text{CH}_3-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-)_{z'}\text{C}(\text{O})-$ and substituted phenyl; wherein Y'' is an n-alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z'' is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent selected from the group consisting of NO_2 , OMe, CN, NMe_2 , OH, CL, Br, and F.
15. A polymer precursor as claimed in claim 13 wherein R'' is $\text{CH}_3\text{C}(\text{O})-$.

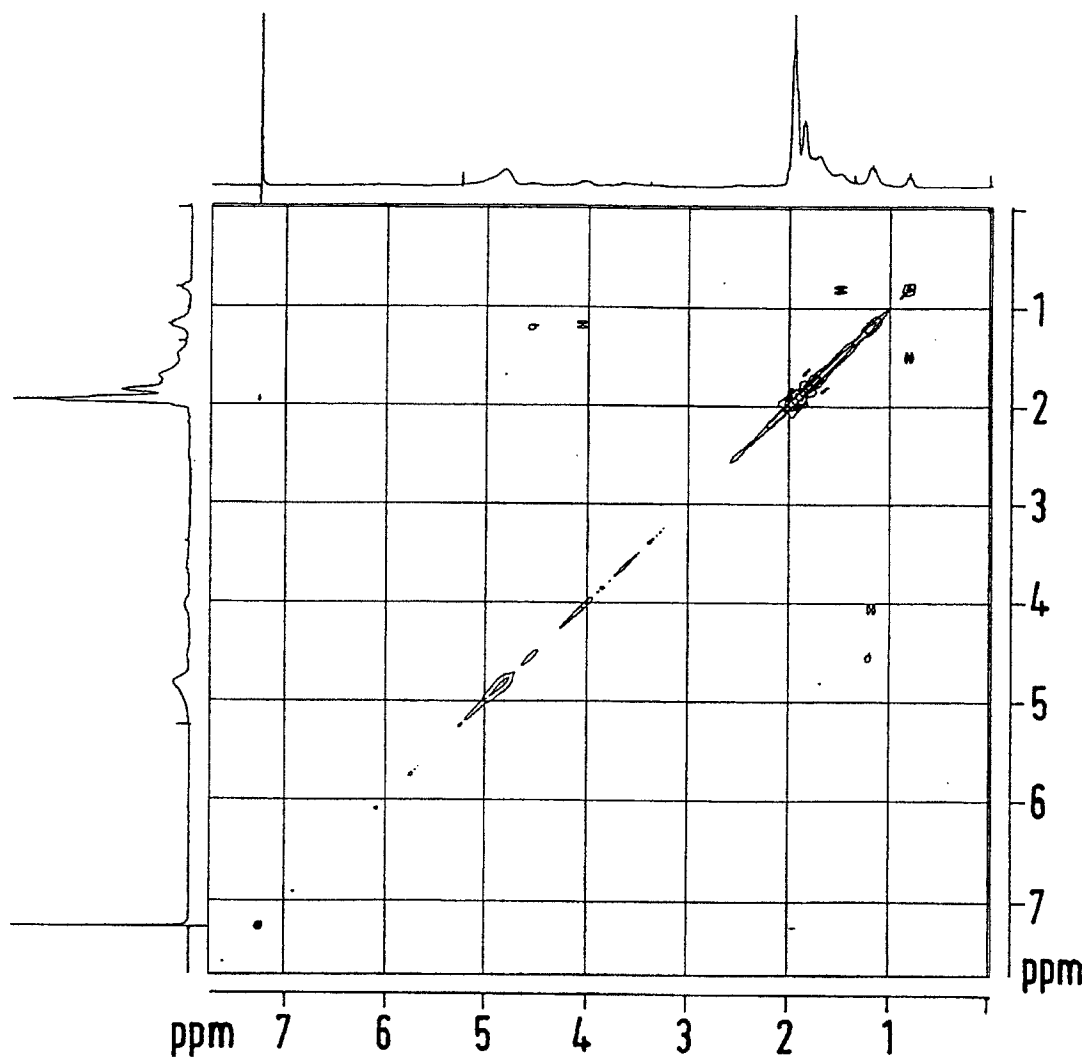
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FIG. 1(a) Example 3



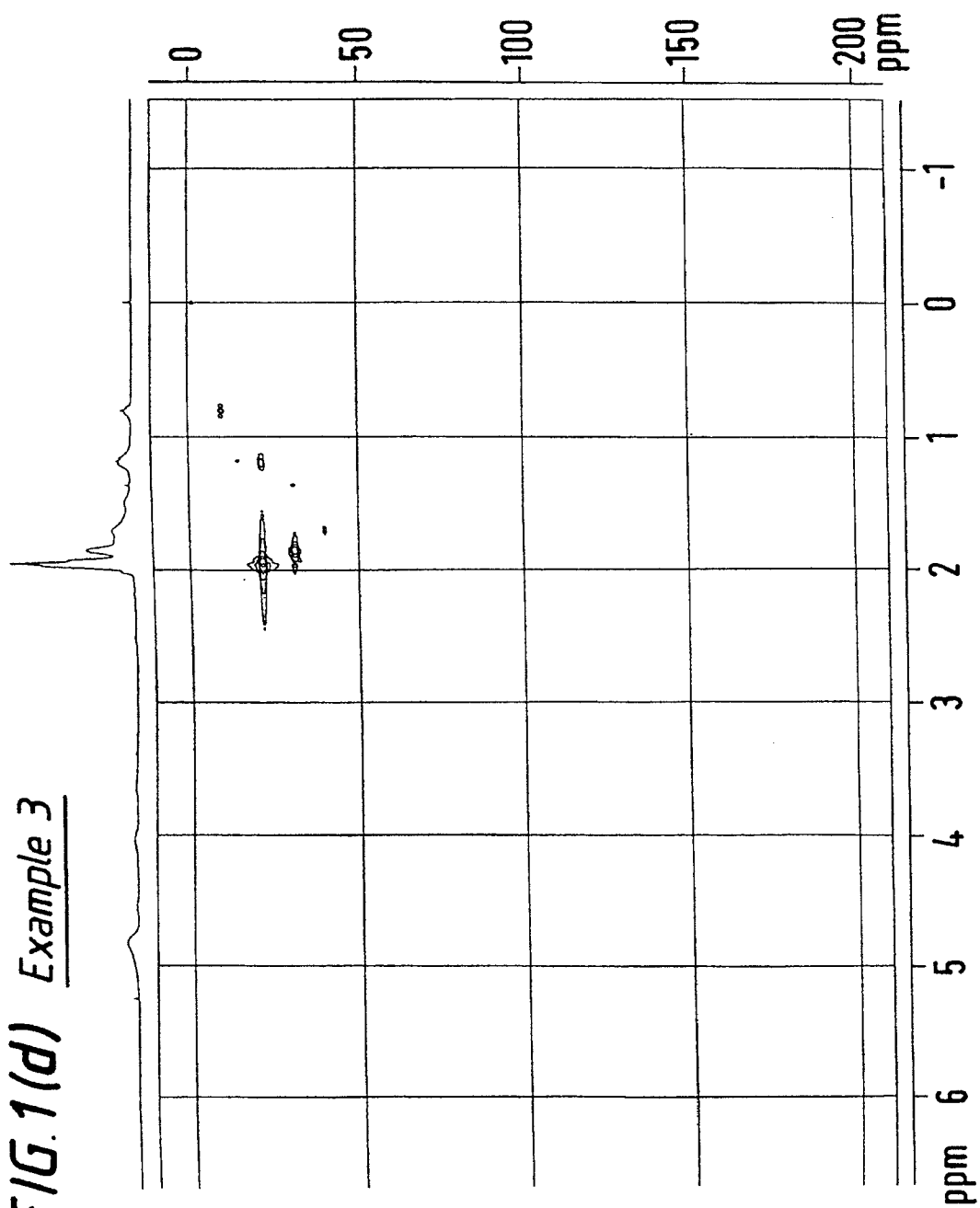


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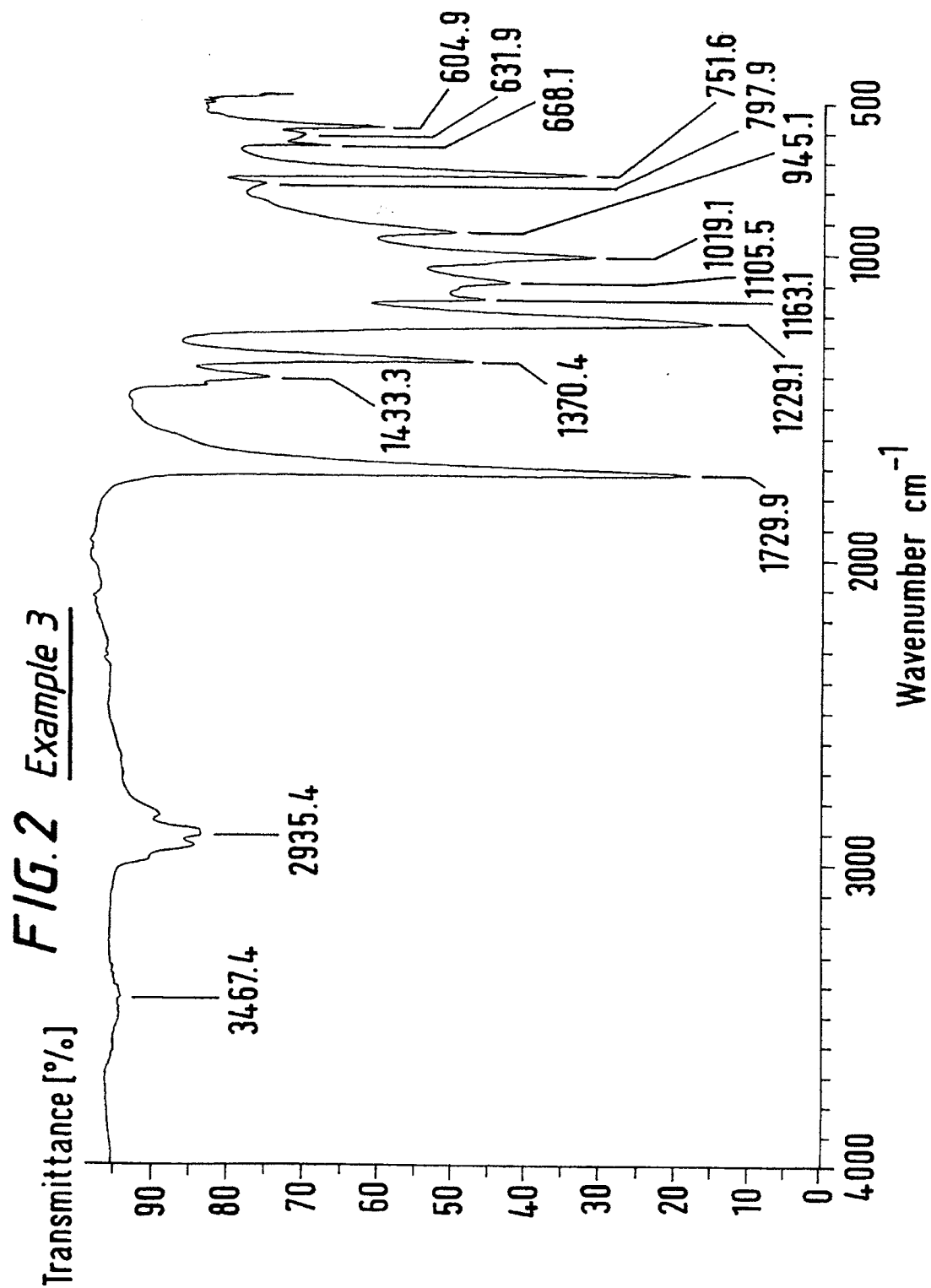
FIG. 1(c) Example 3

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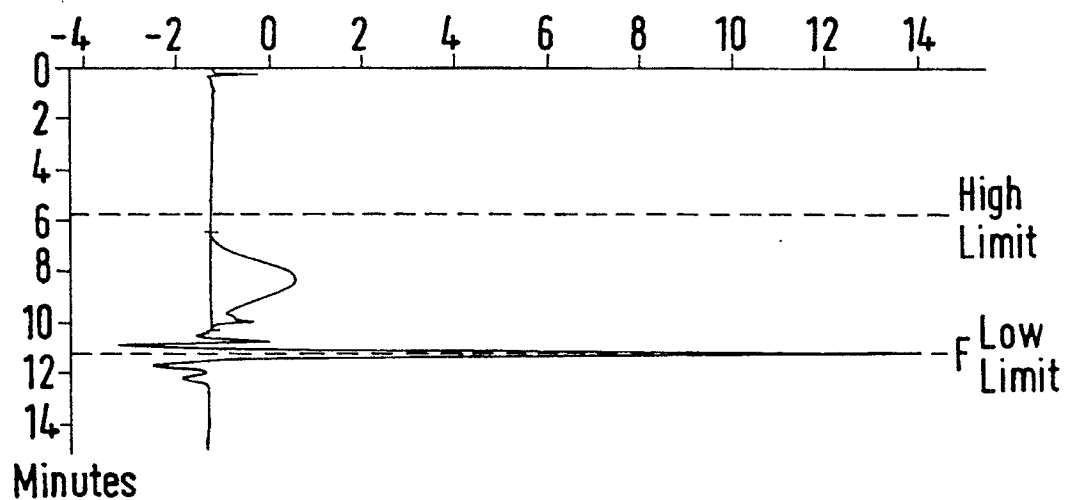
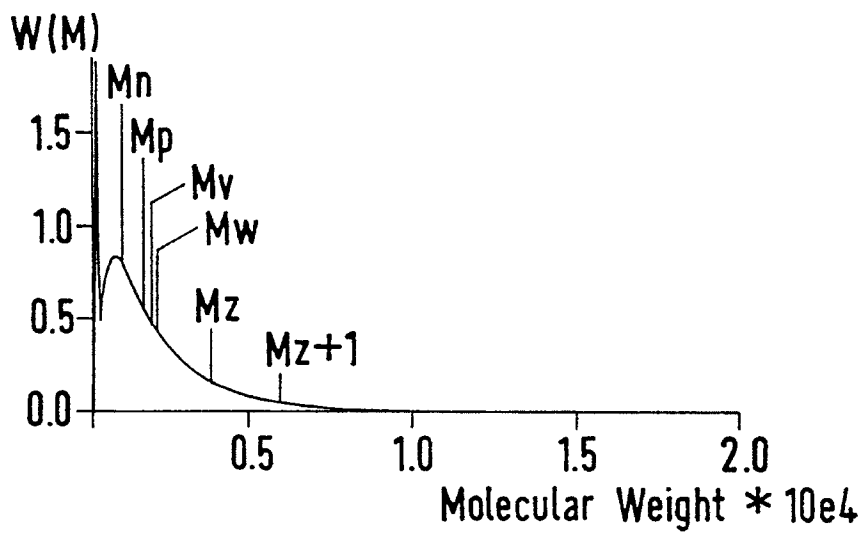
FIG. 1(d) Example 3



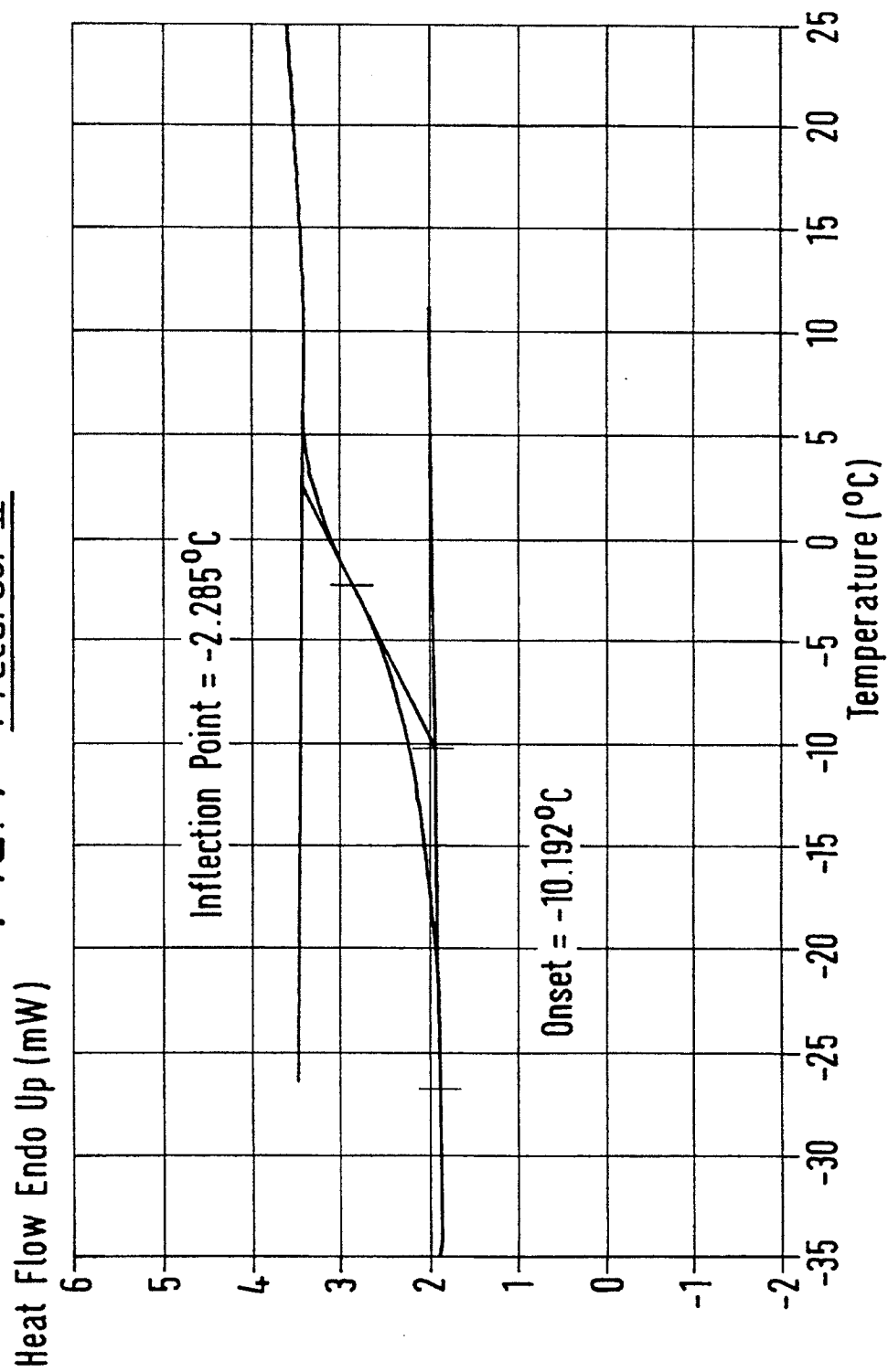
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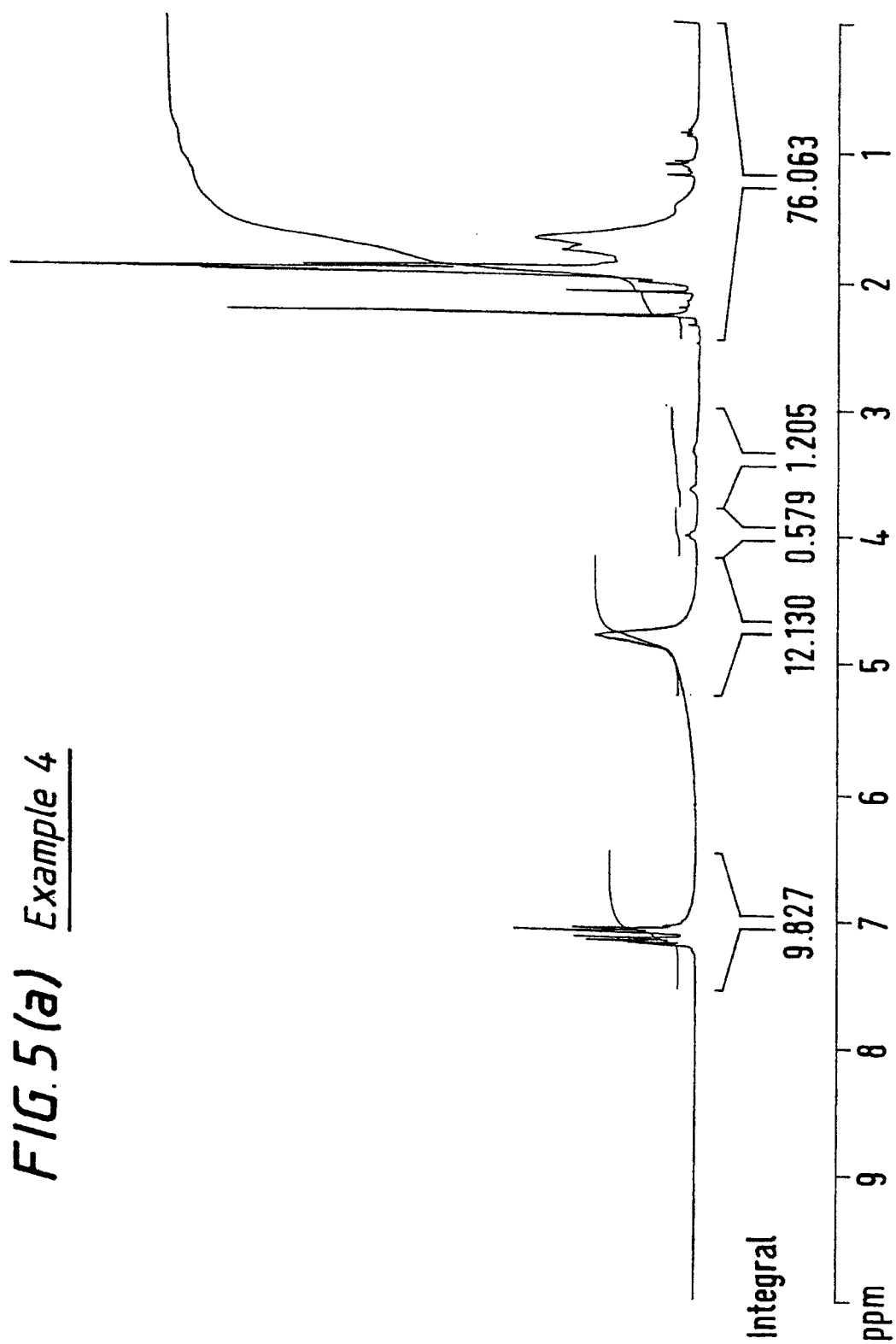
FIG.3 Example 3*Raw Chromatogram:**W(M) plot:*

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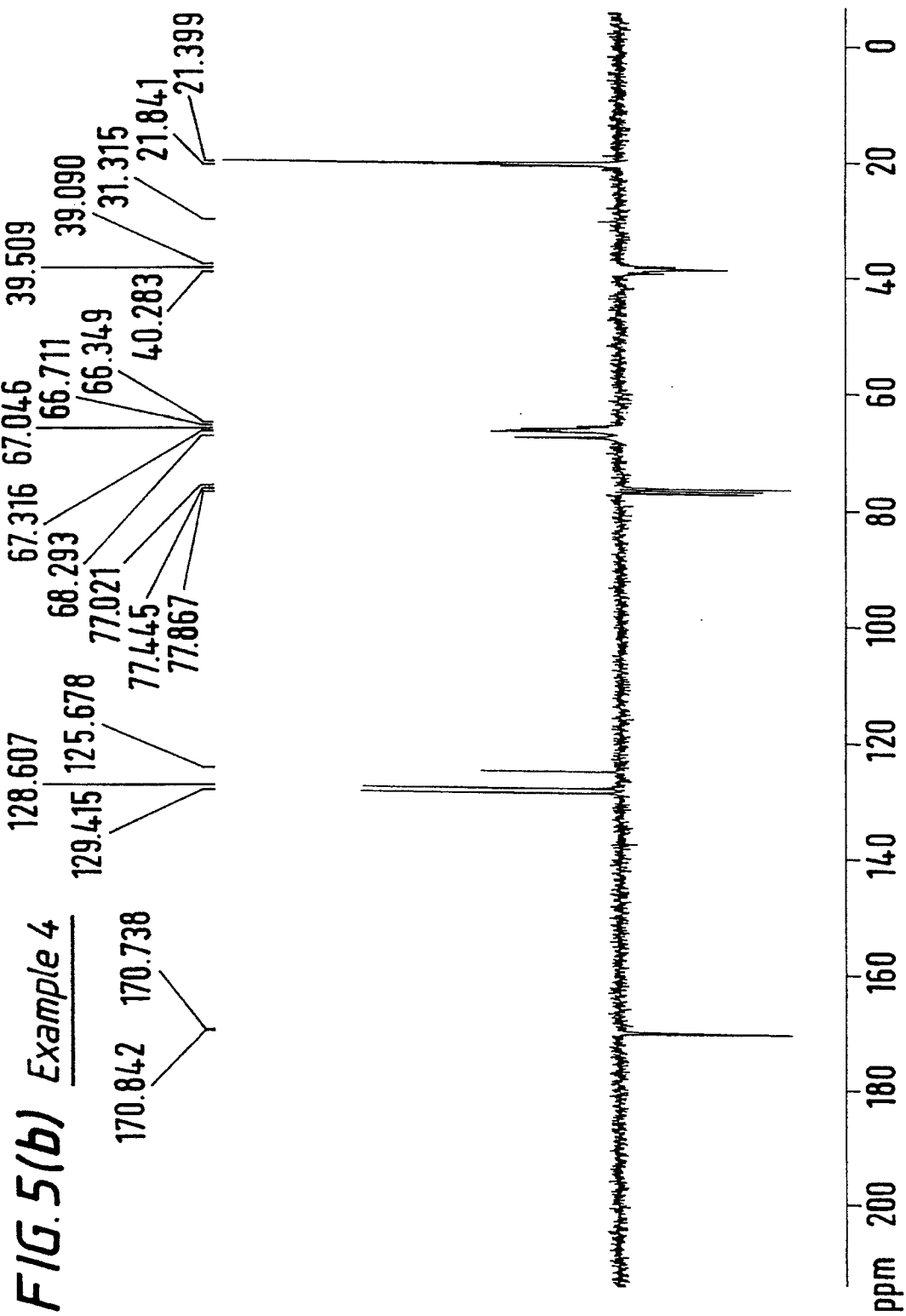
FIG. 4 Precursor II

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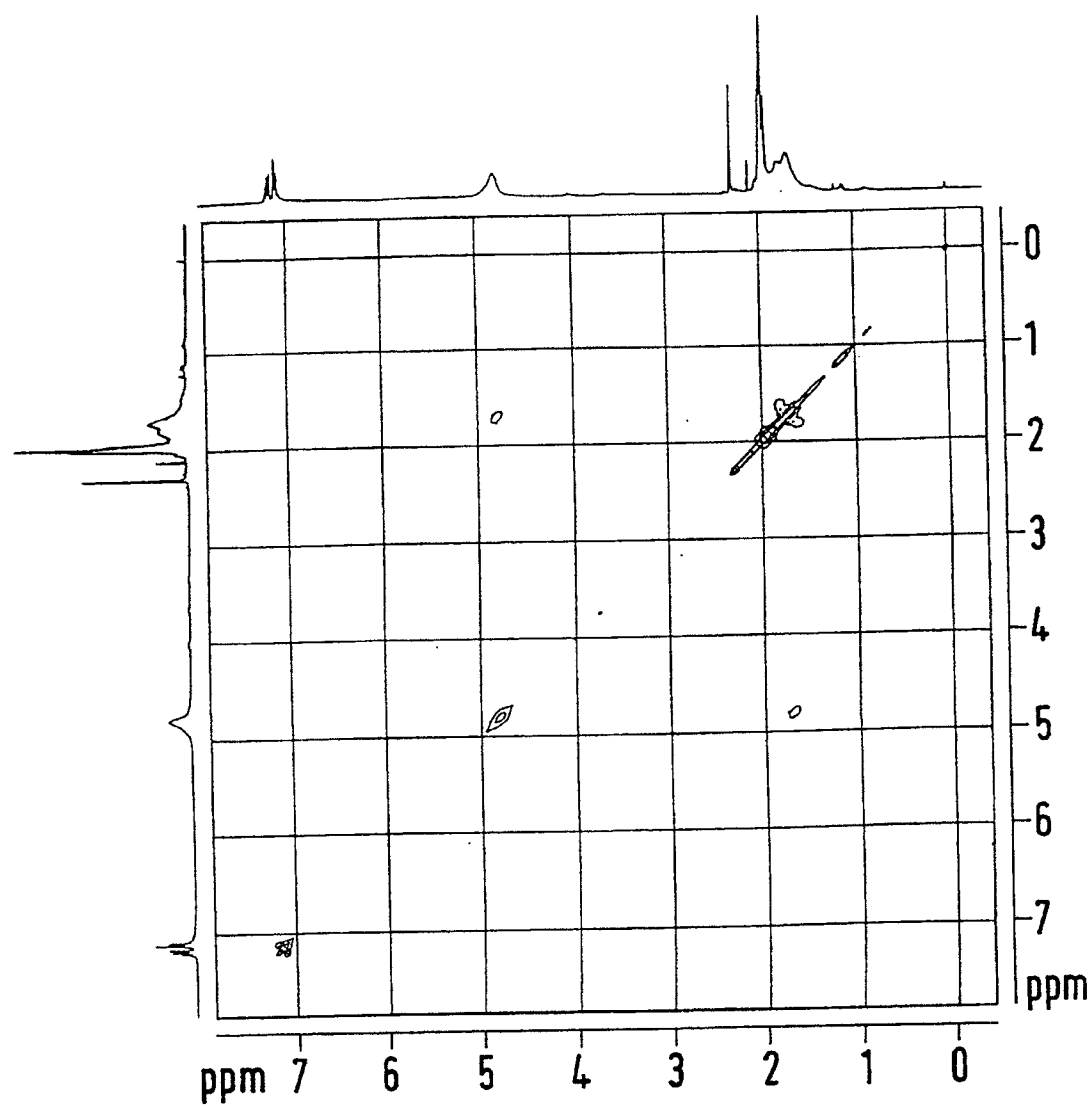
FIG. 5(a) Example 4



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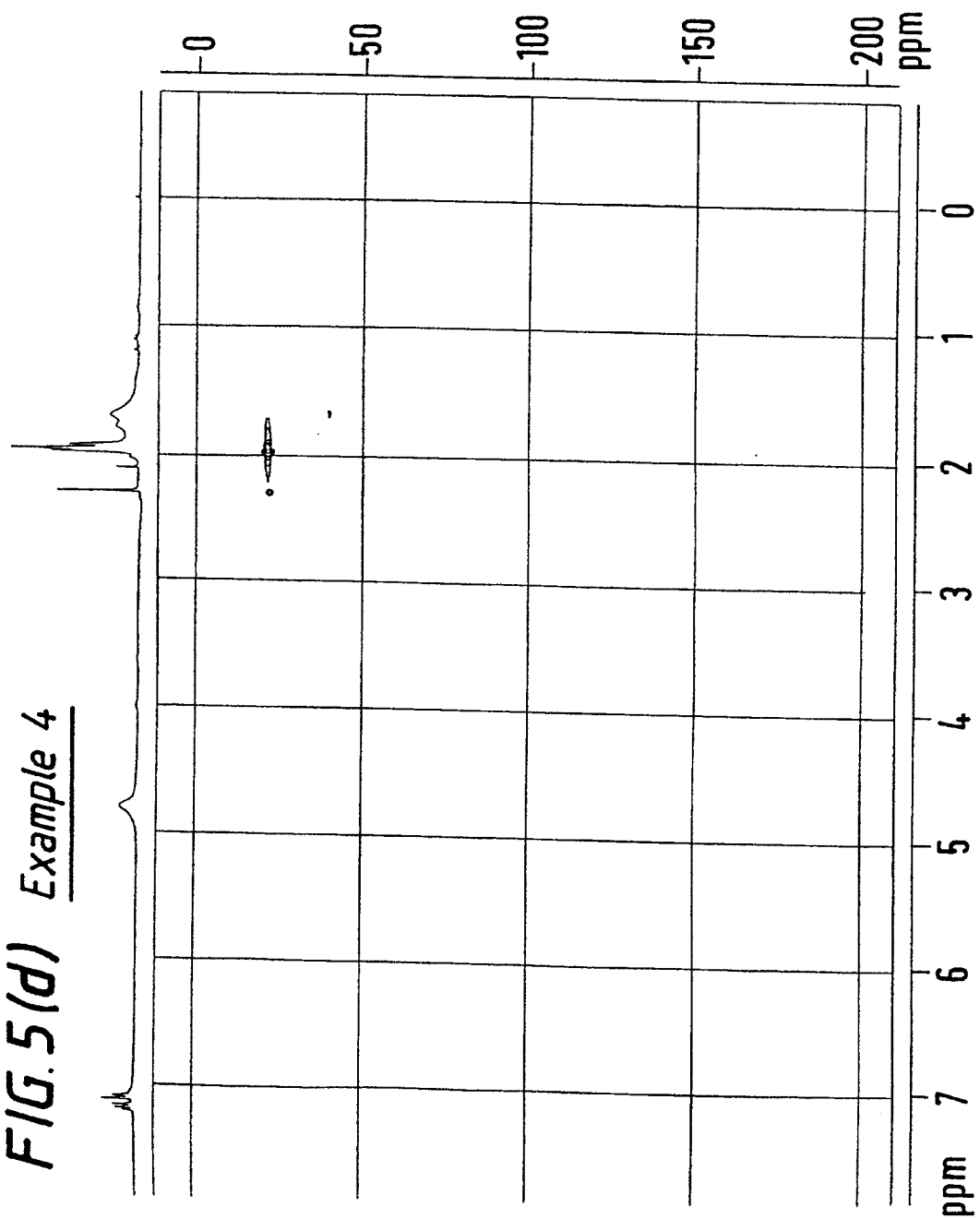


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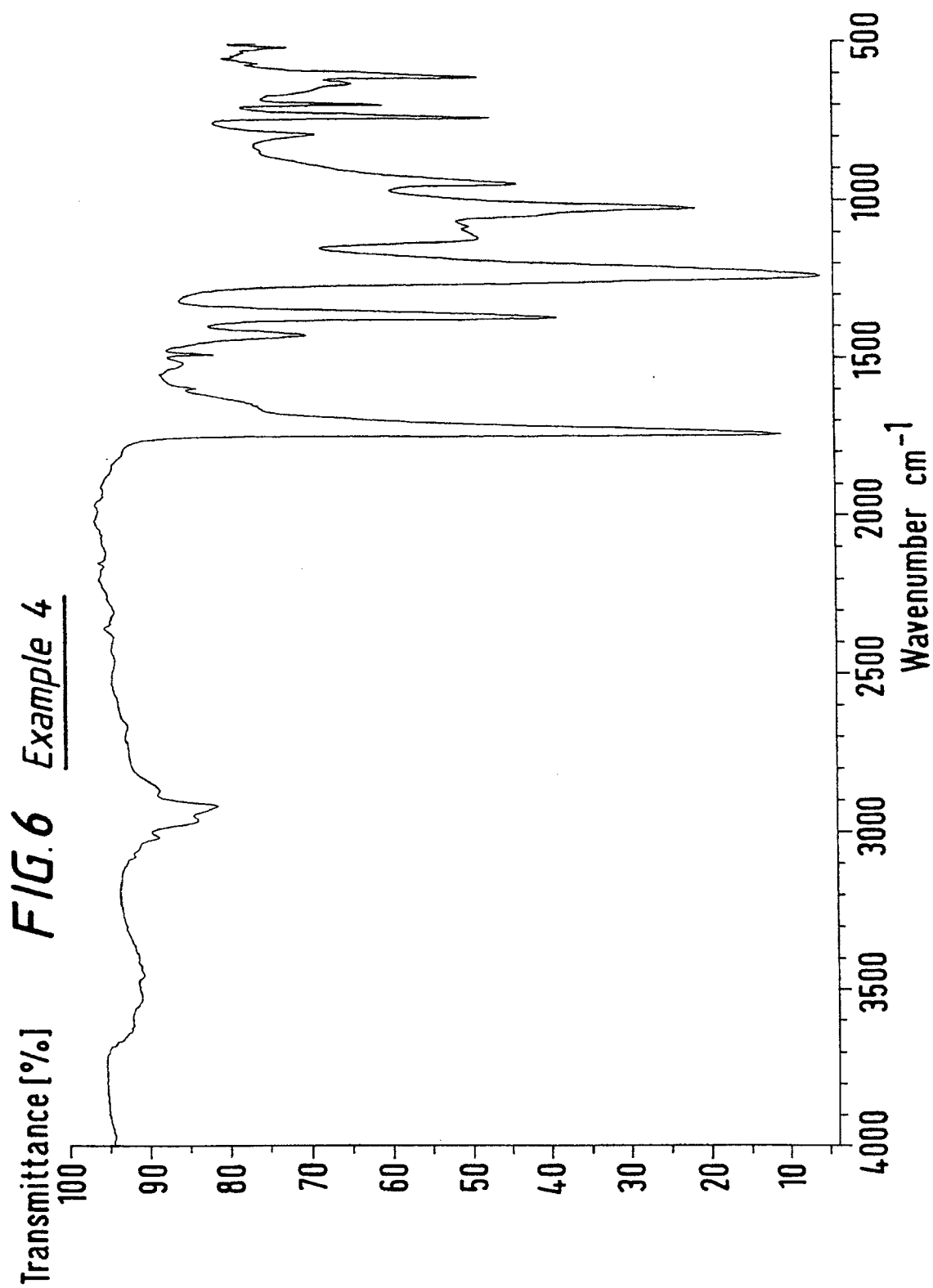
FIG. 5(c) Example 4

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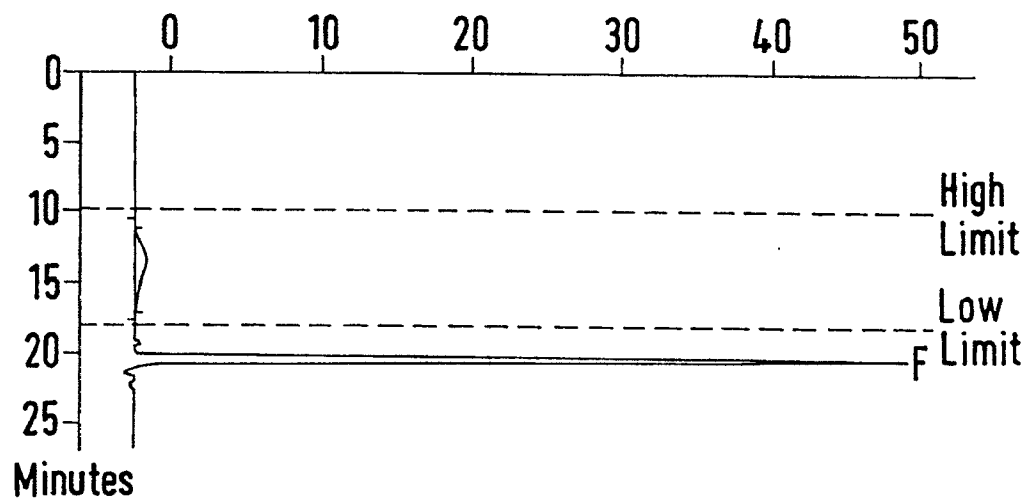
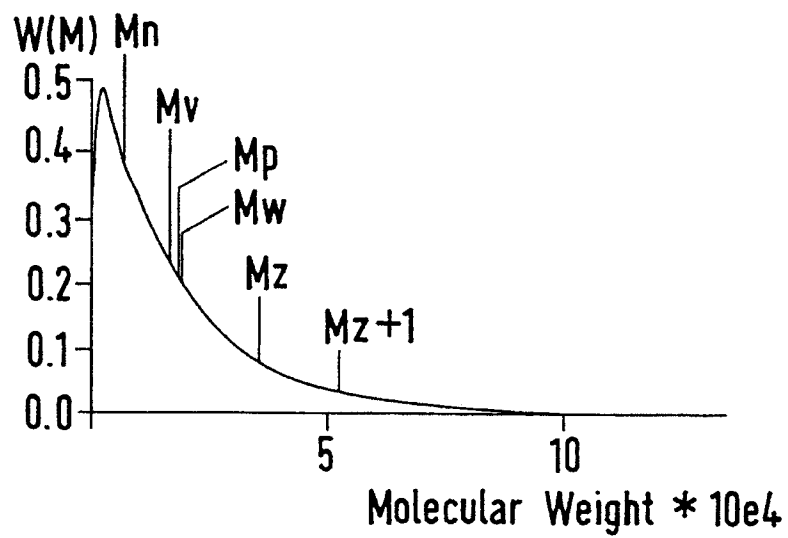
FIG. 5(d) Example 4



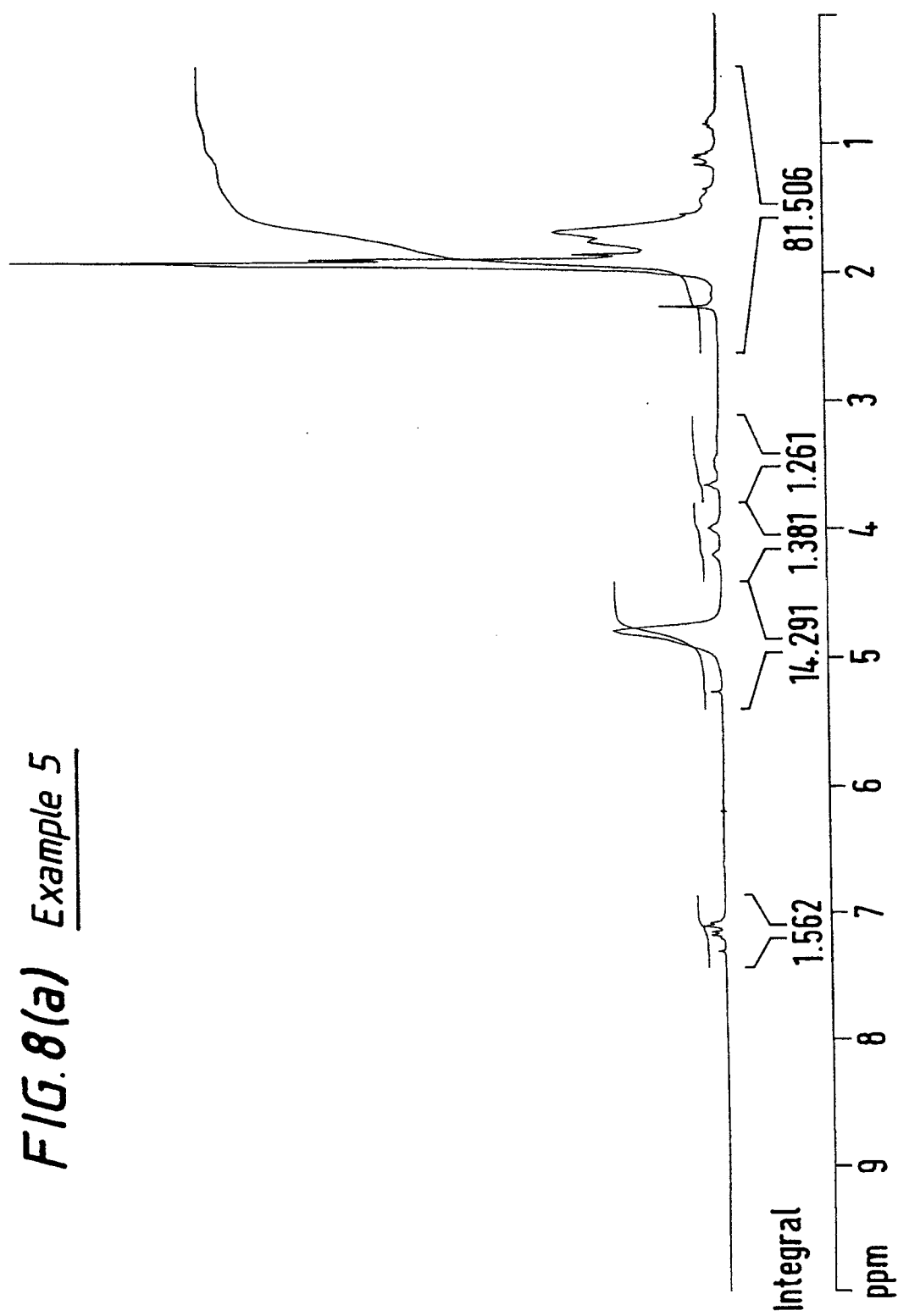
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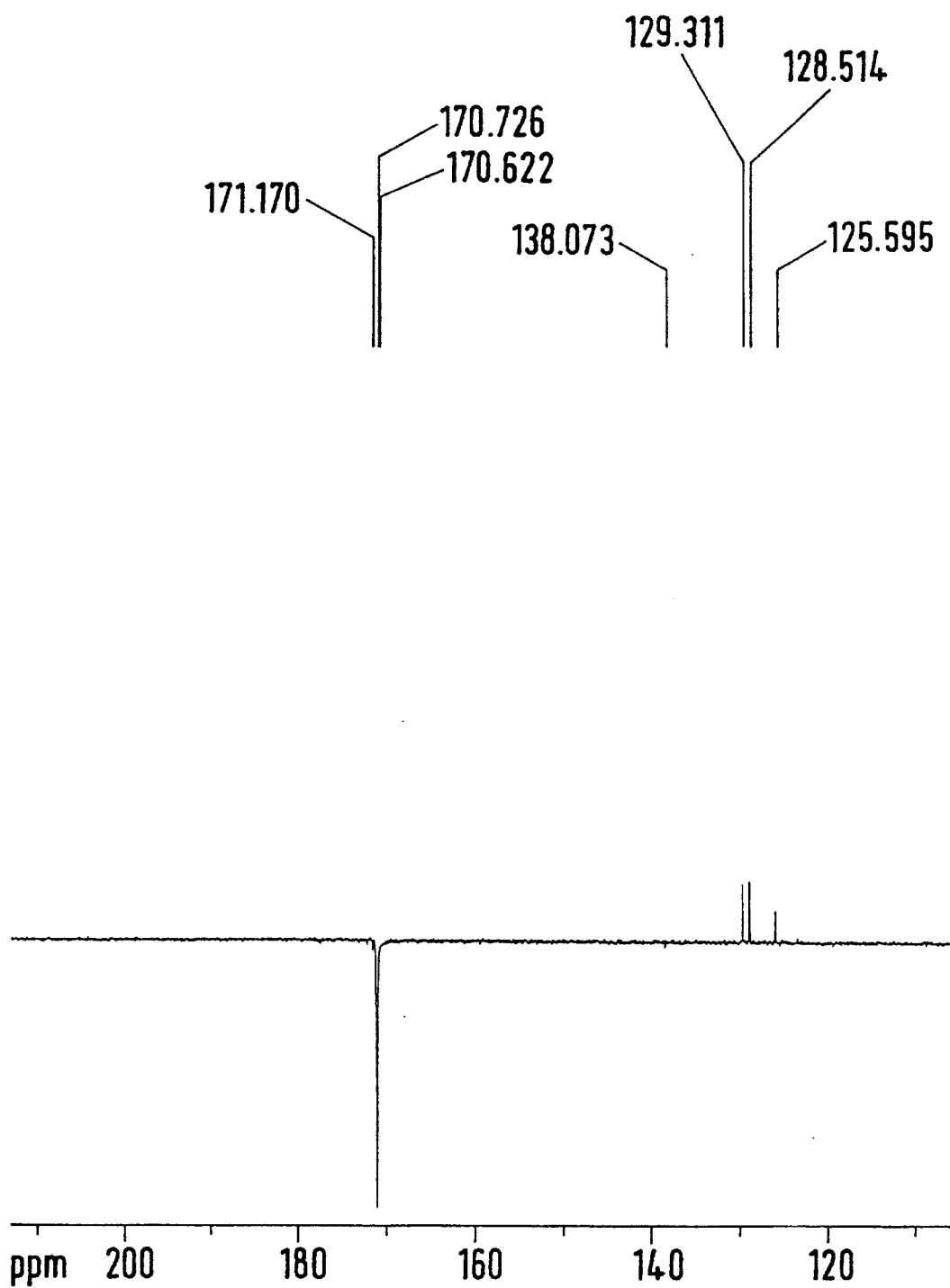
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FIG.7 Example 4*Raw Chromatogram:**W(M) plot:*

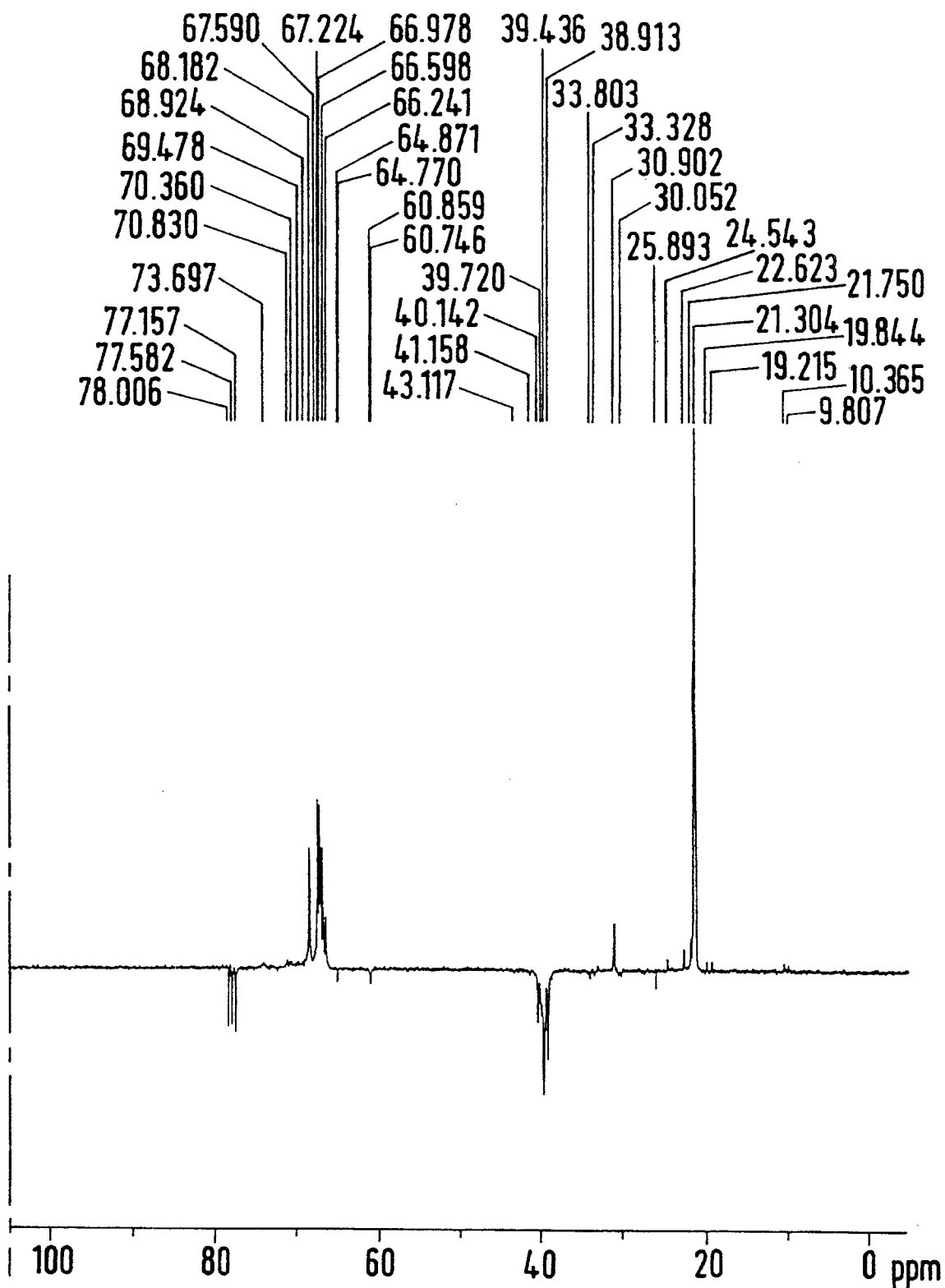
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FIG. 8(a) Example 5

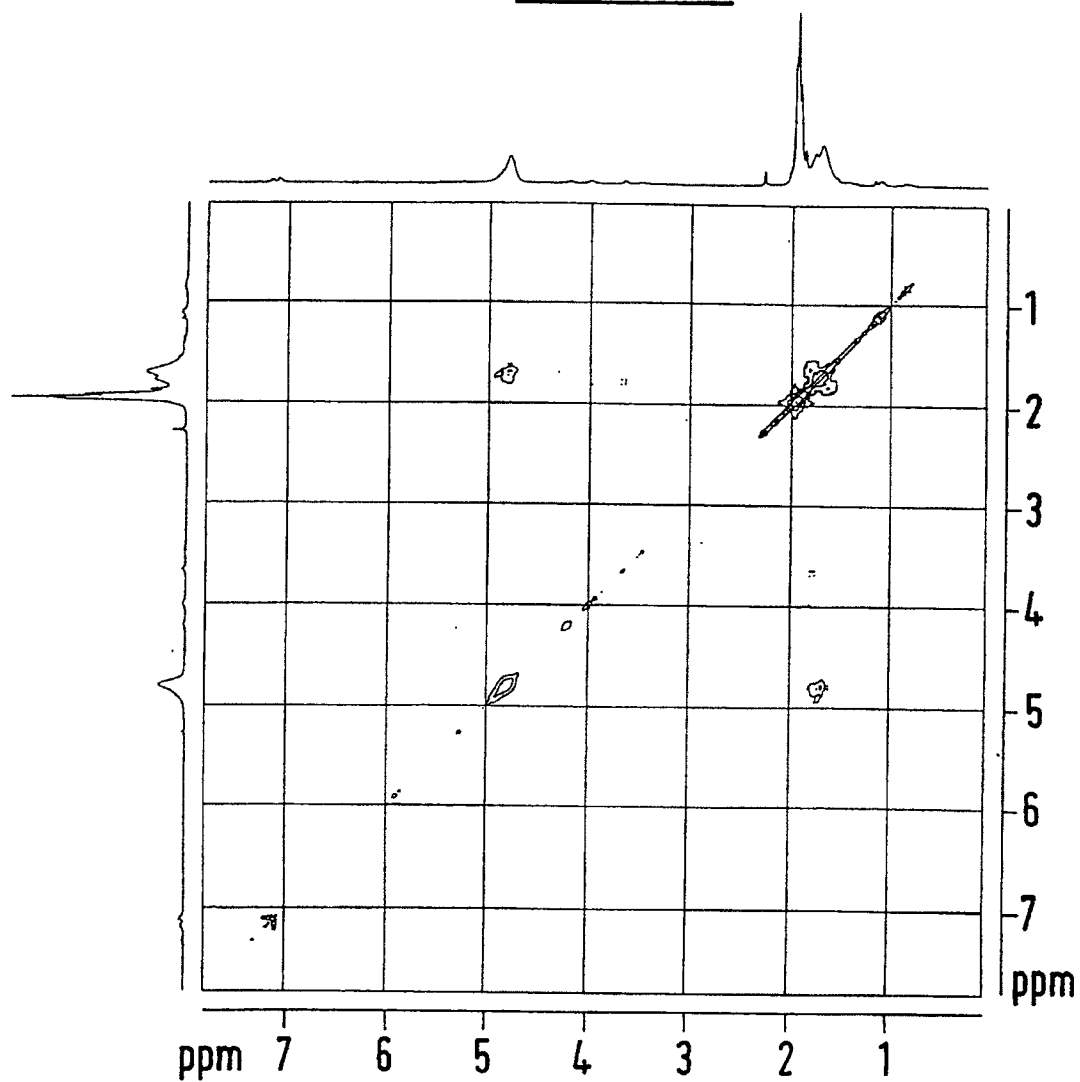
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FIG. 8(b') Example 5

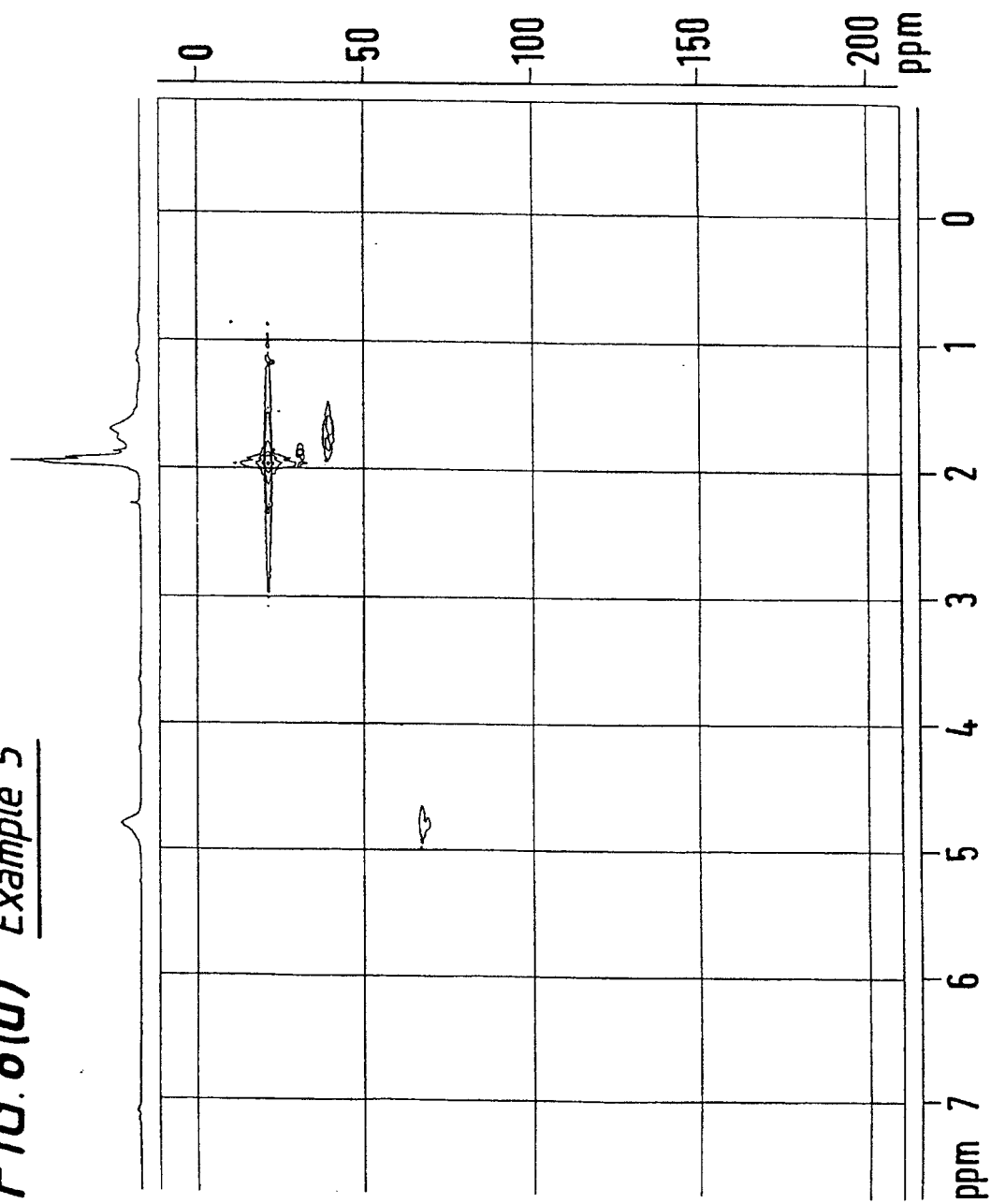
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FIG. 8(b'') Example 5

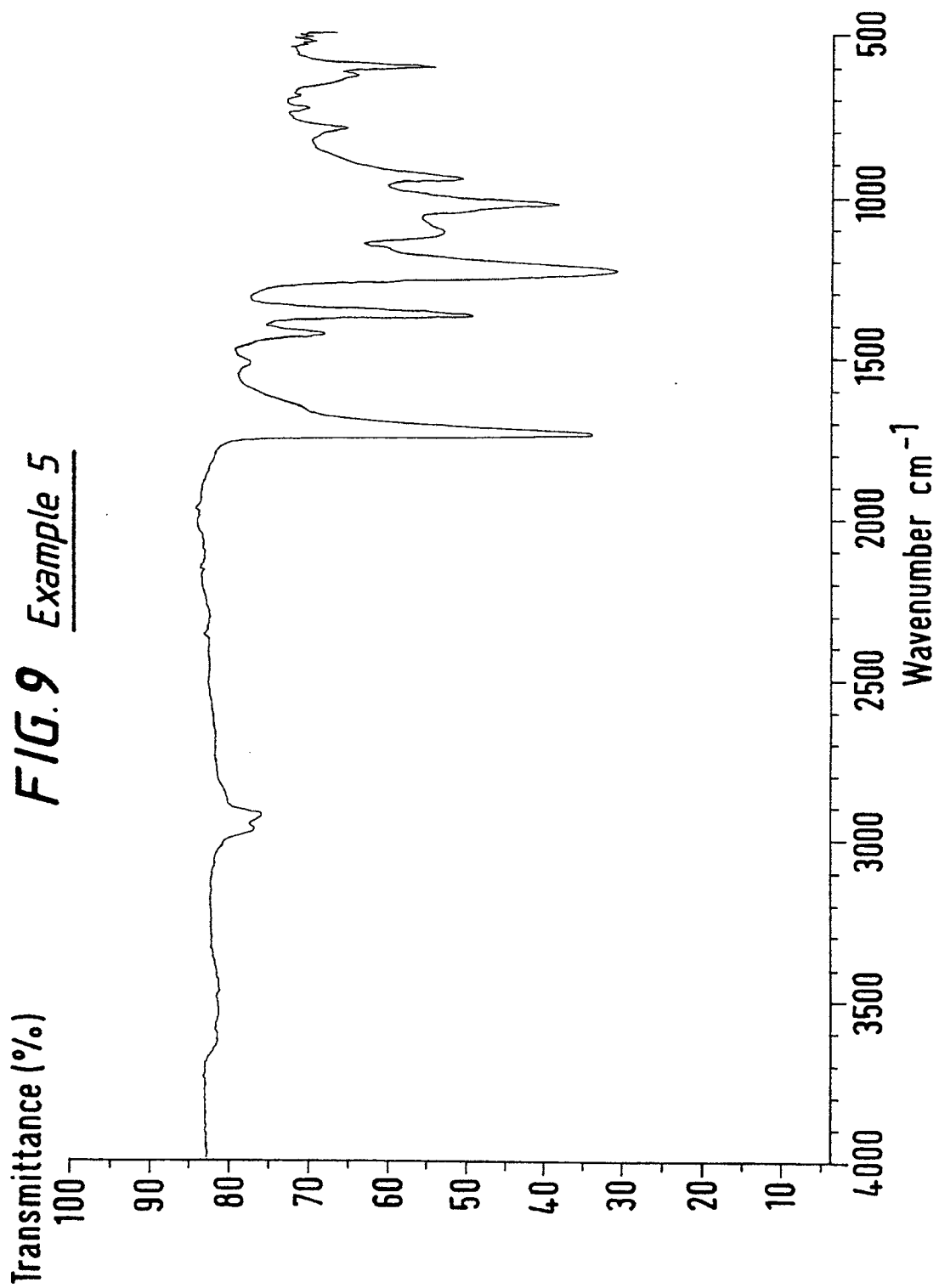
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FIG. 8(c) Example 5

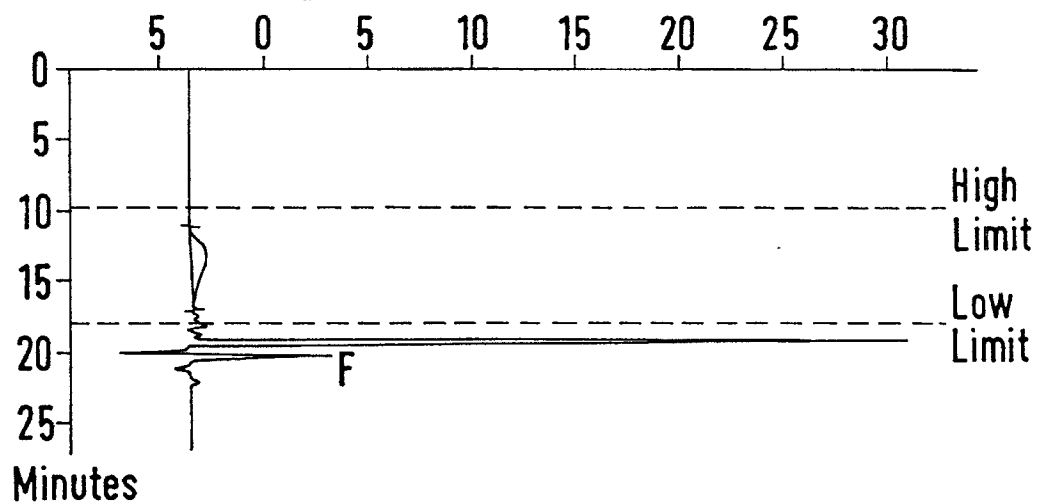
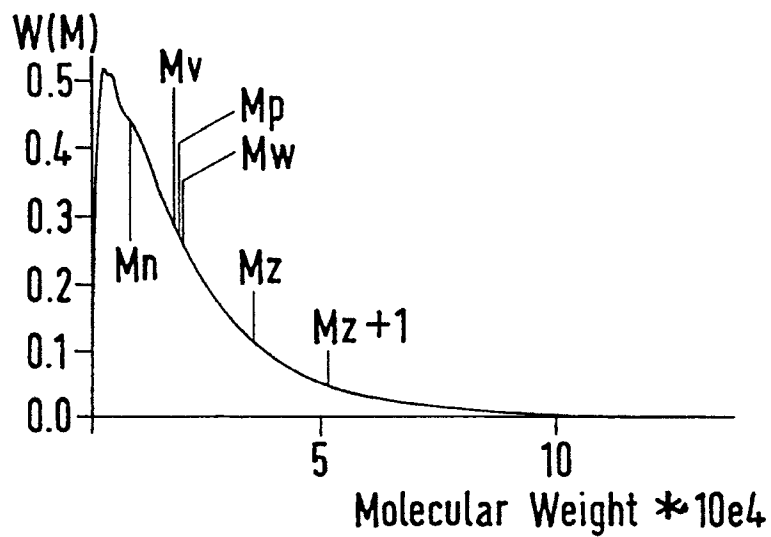
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FIG. 8(d) Example 5

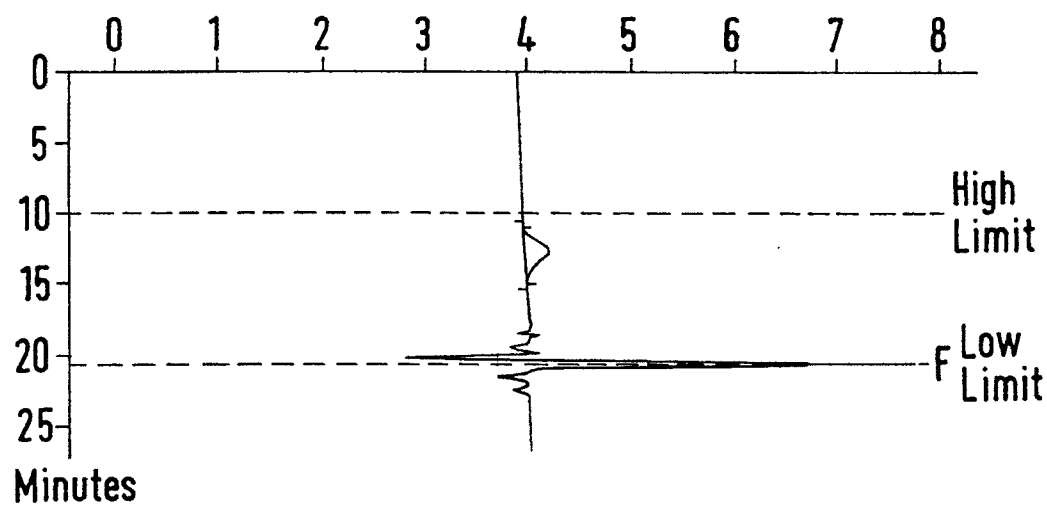
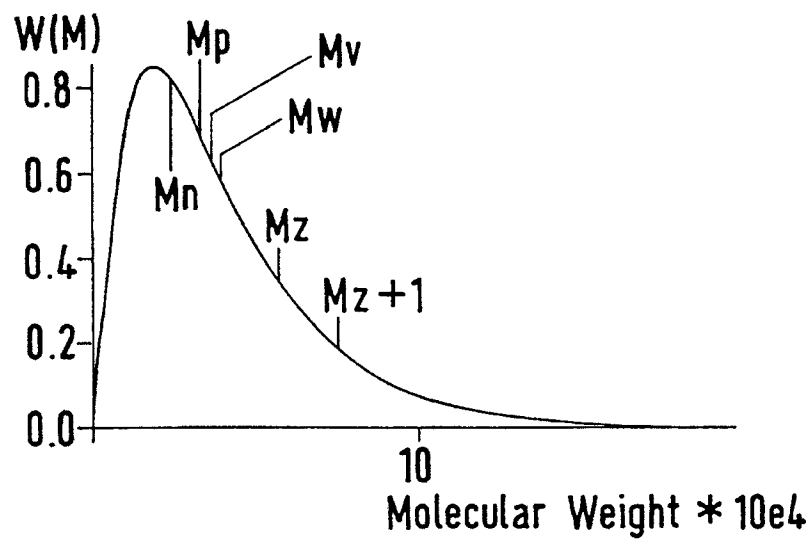
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FIG. 9 Example 5

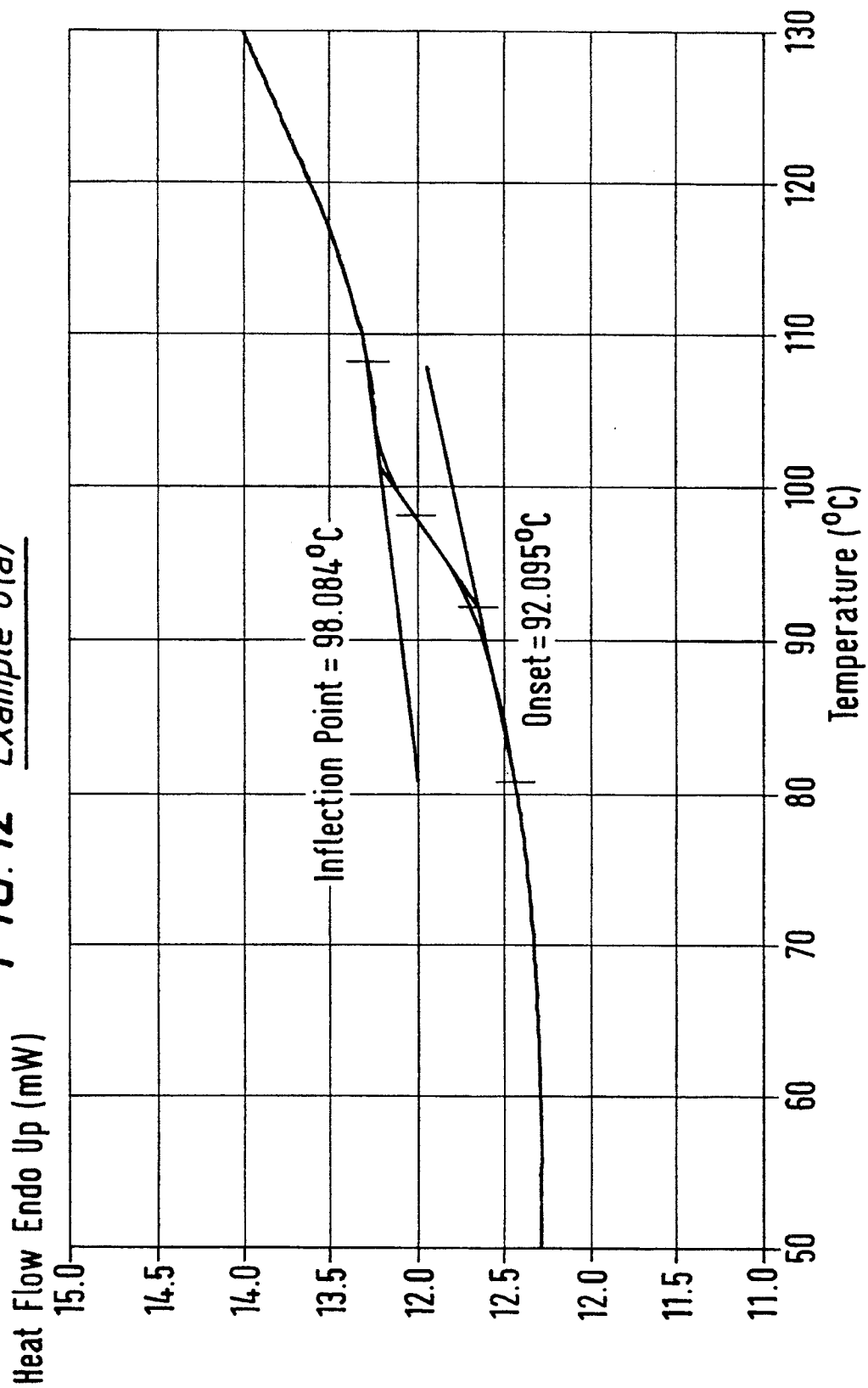
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FIG. 10 Example 5*Raw Chromatogram:**W(M) plot:*

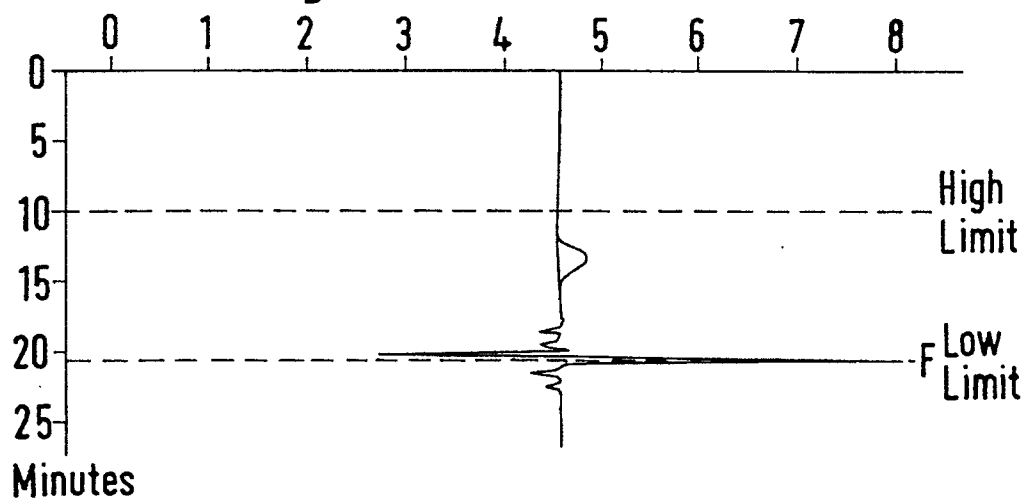
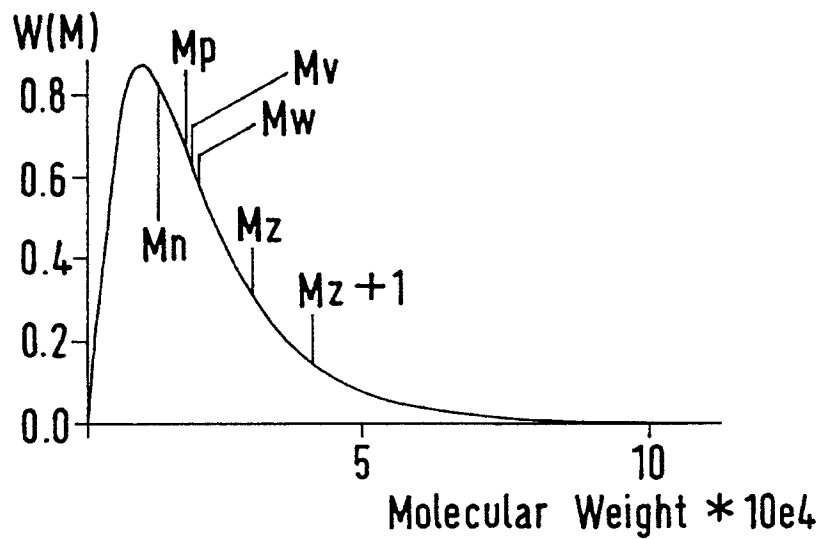
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FIG. 11 *Example 6(a)**Raw Chromatogram:**W(M) plot:*

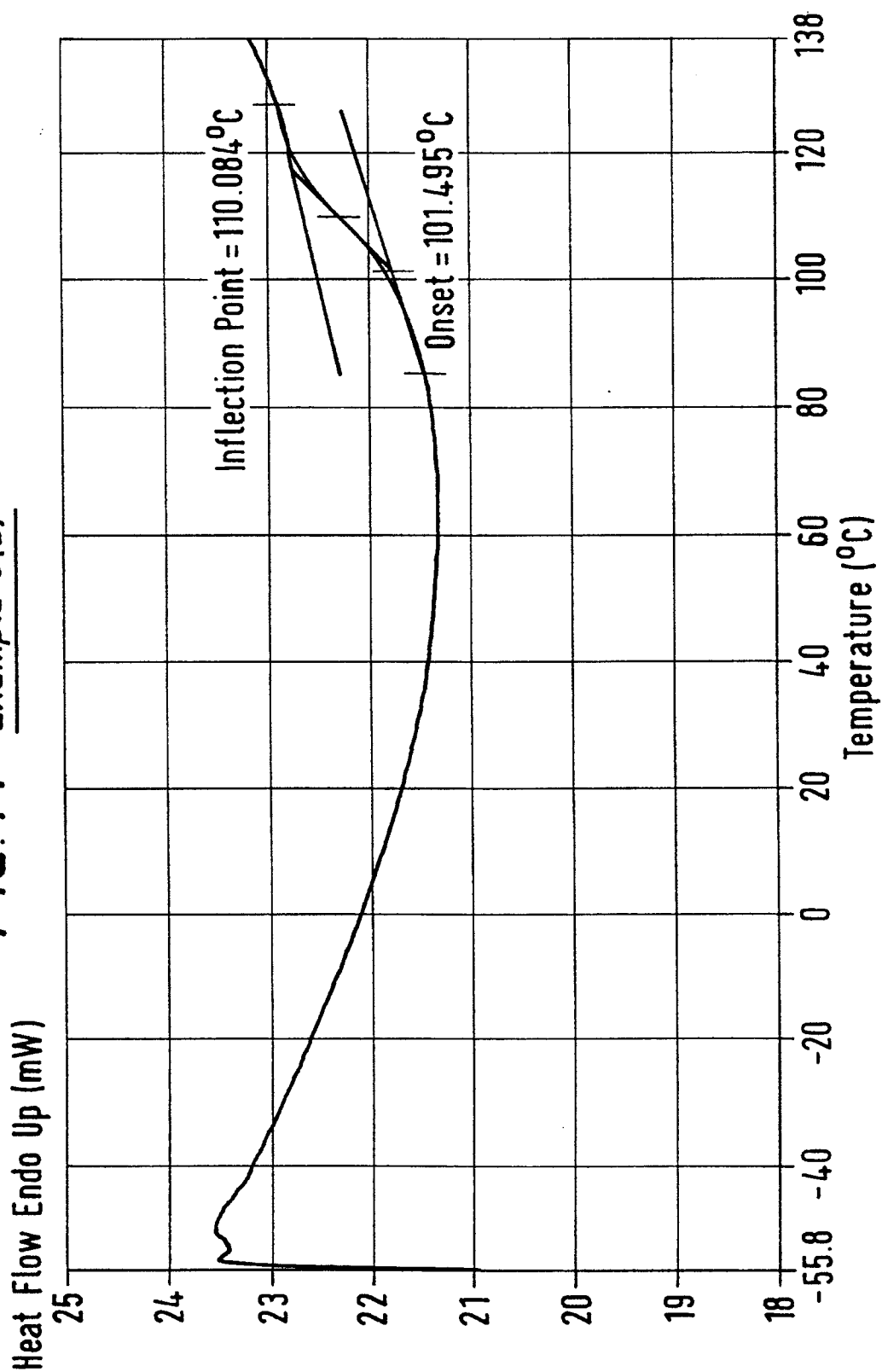
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FIG. 12 Example 6(a)

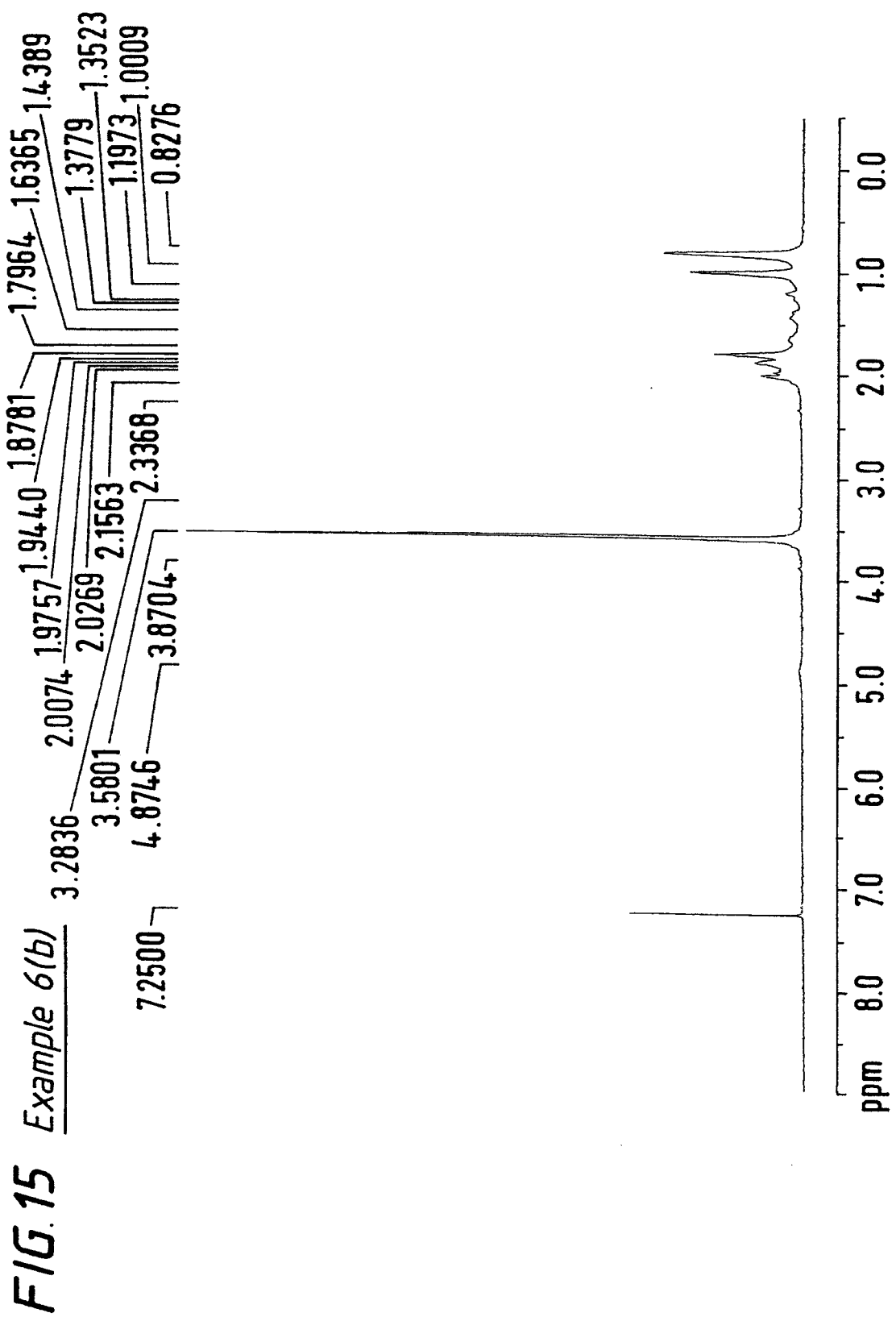
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FIG. 13 Example 6(b)*Raw Chromatogram:**W(M) plot:*

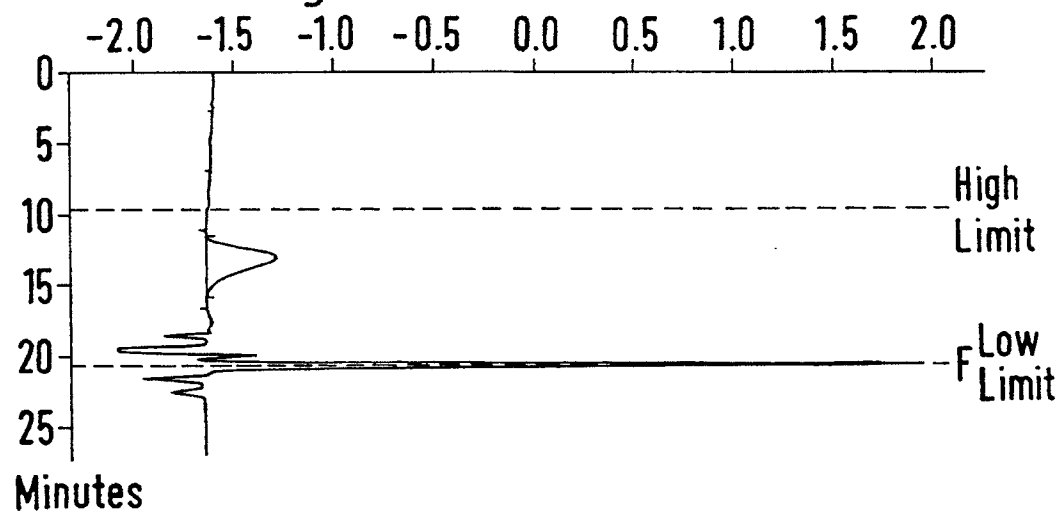
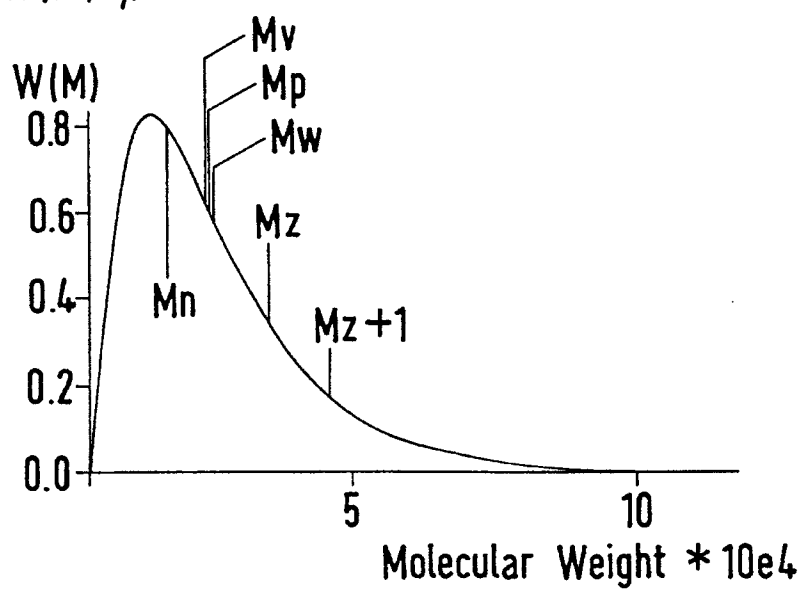
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FIG. 14 Example 6(b)

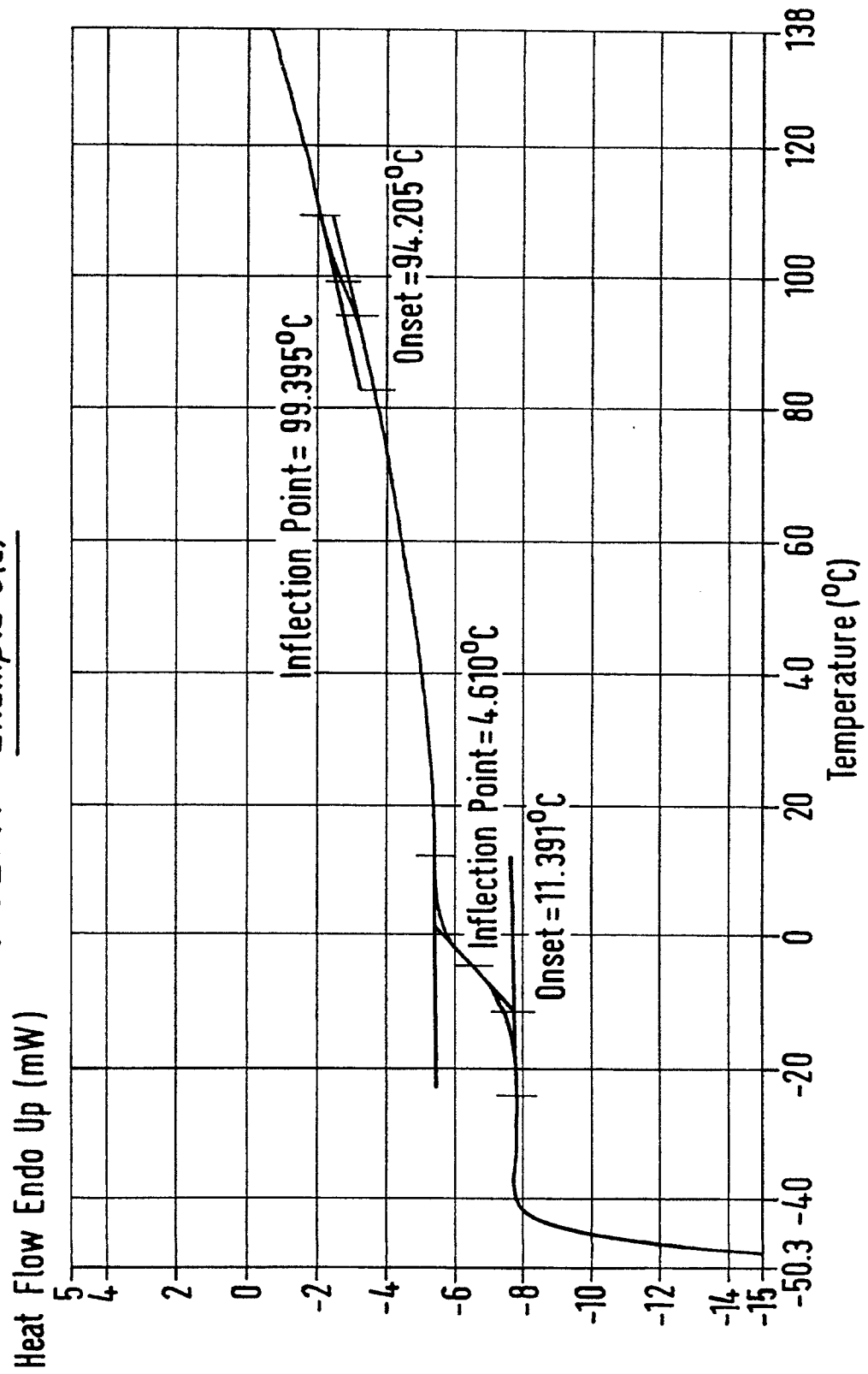
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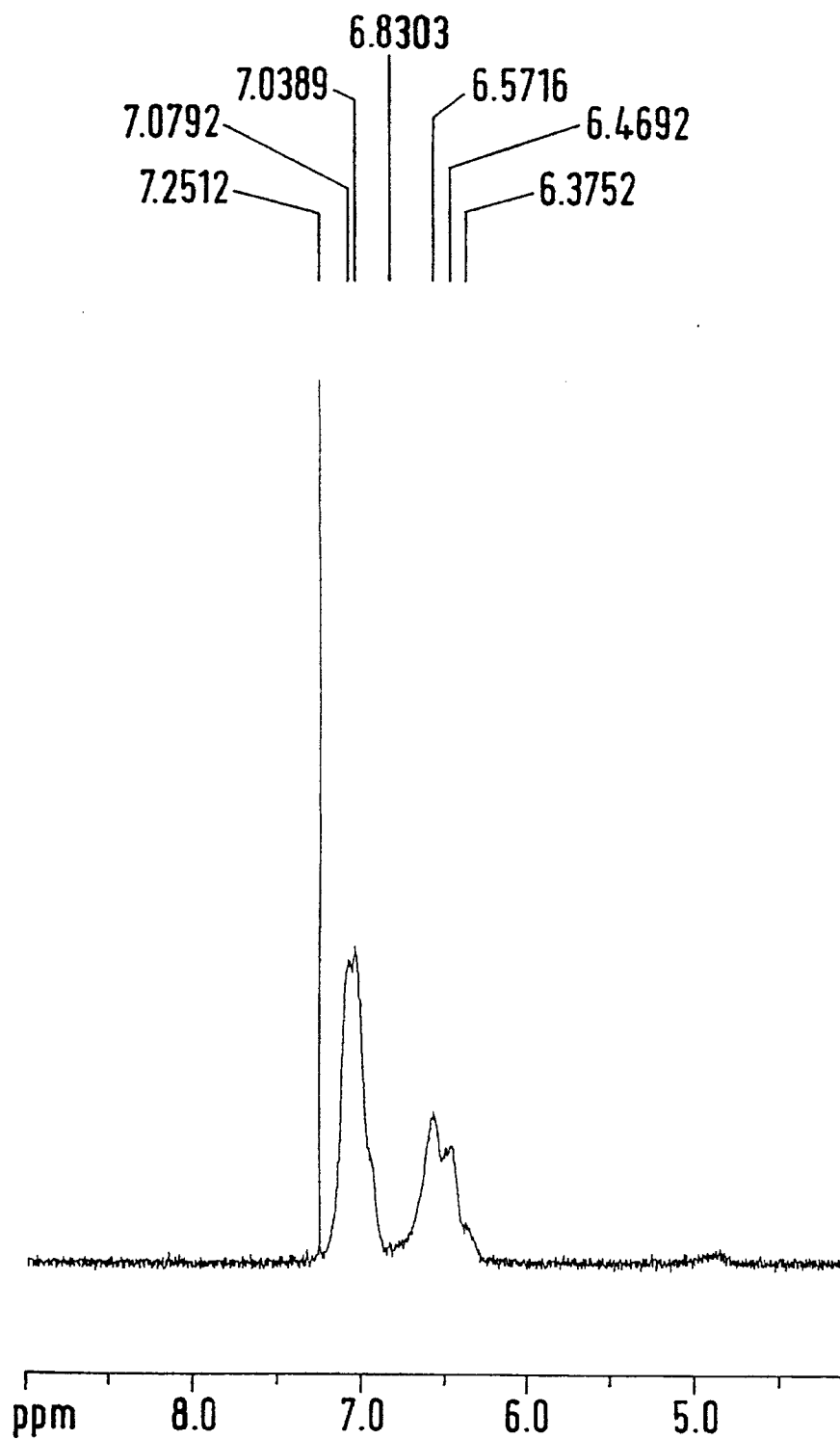
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FIG.16 Example 6(c)*Raw Chromatogram:**W(M) plot:*

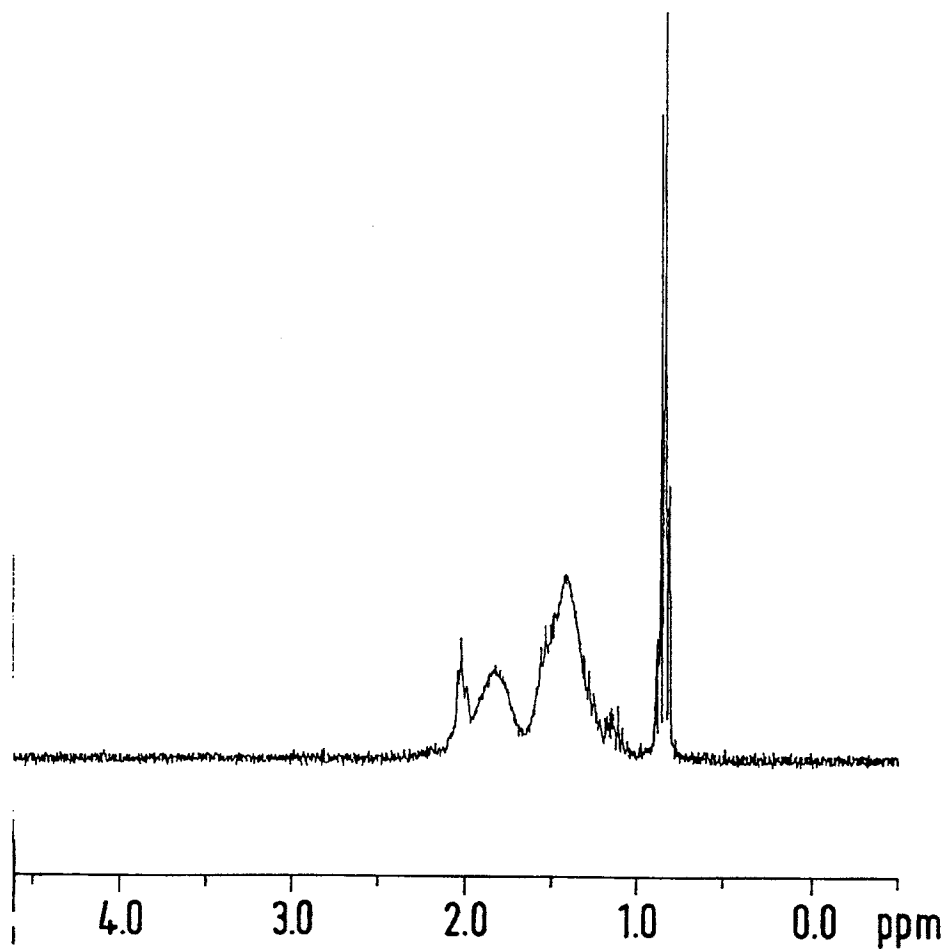
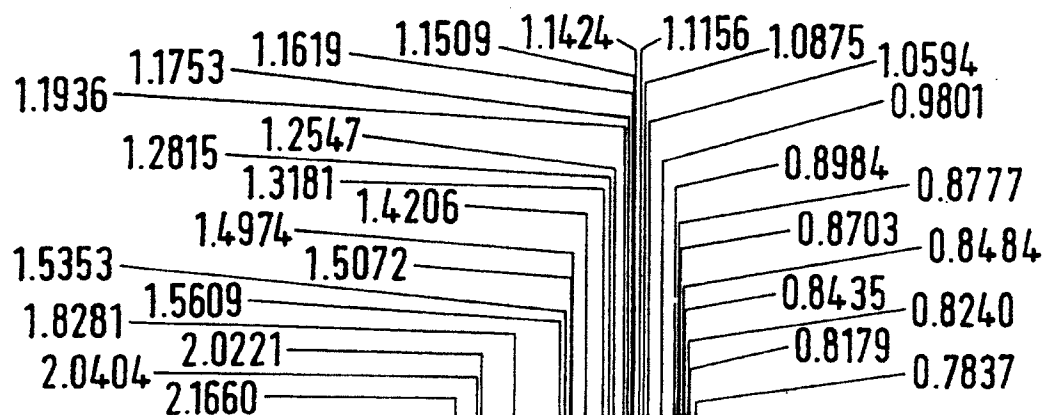
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FIG. 17 Example 6(c)

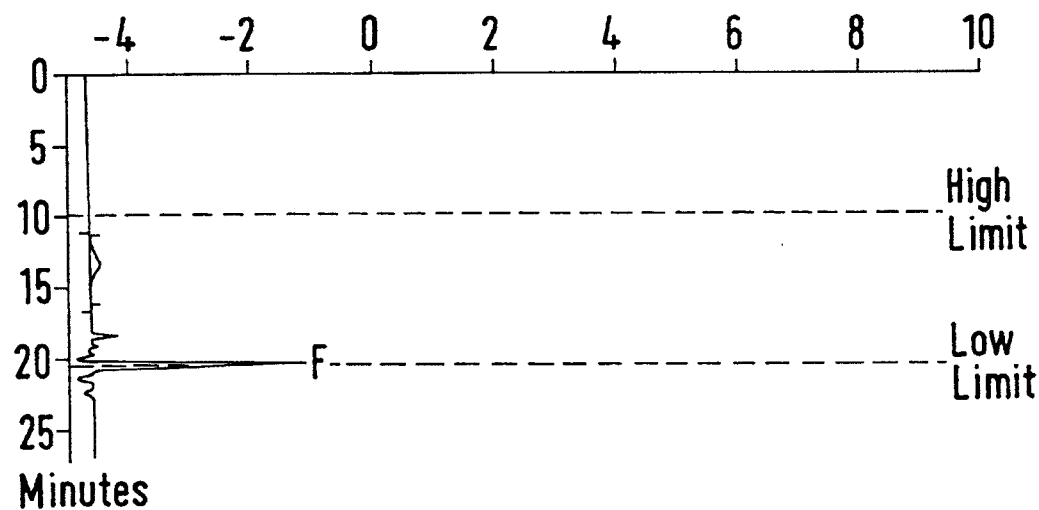
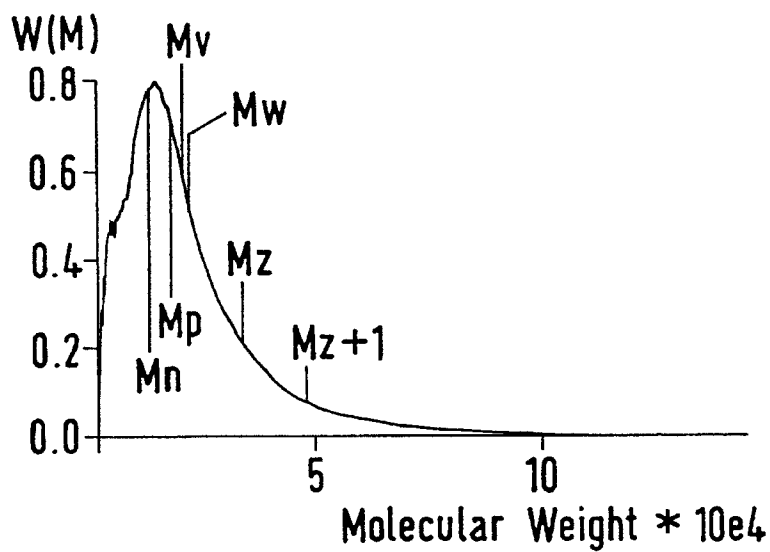
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FIG. 18' Example 6(c)

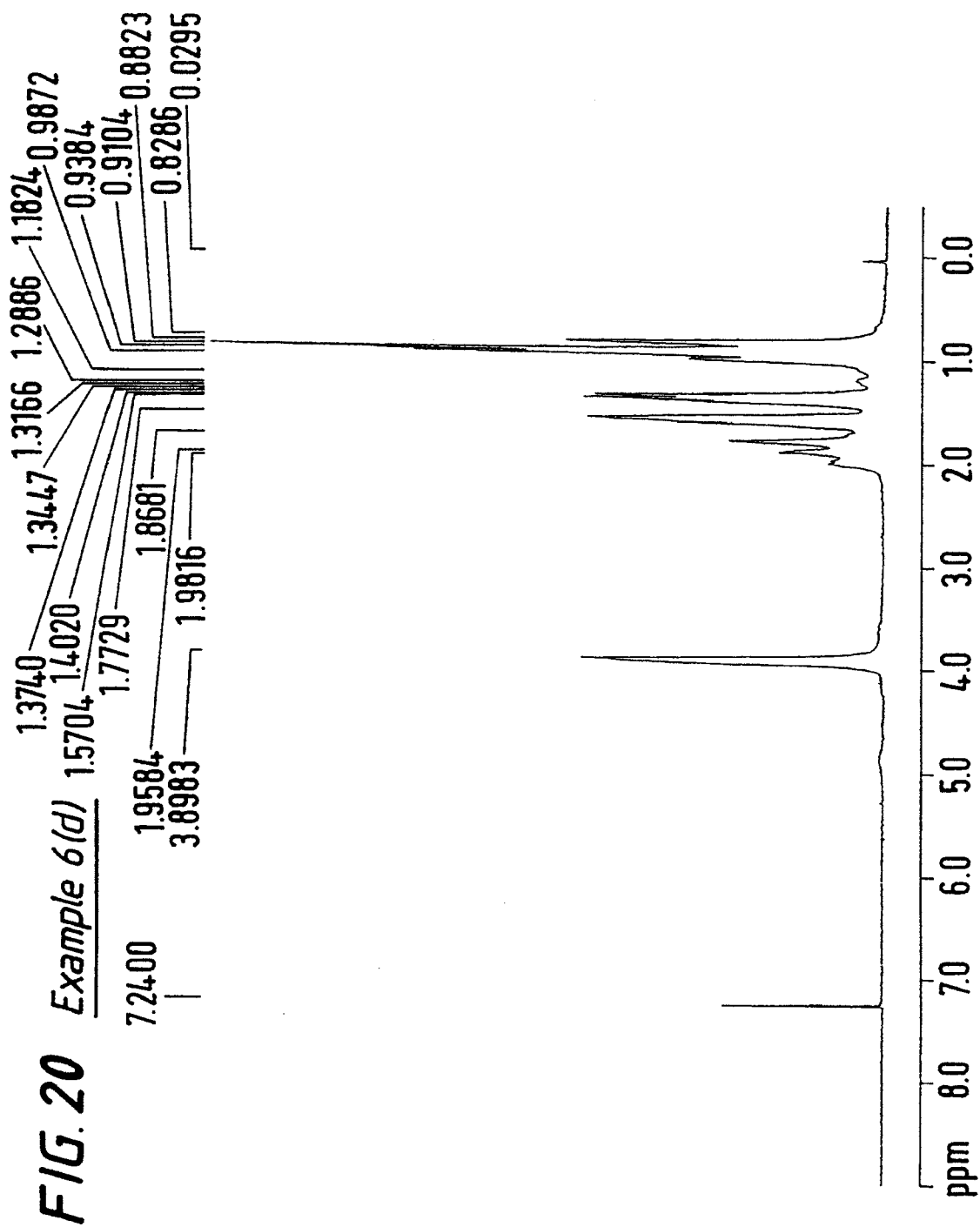
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FIG. 18^{II} Example 6(c)

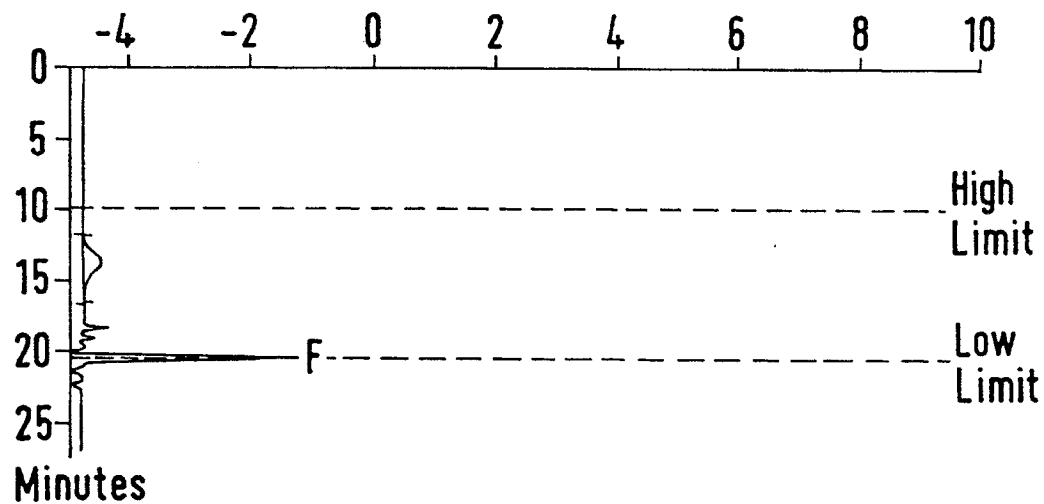
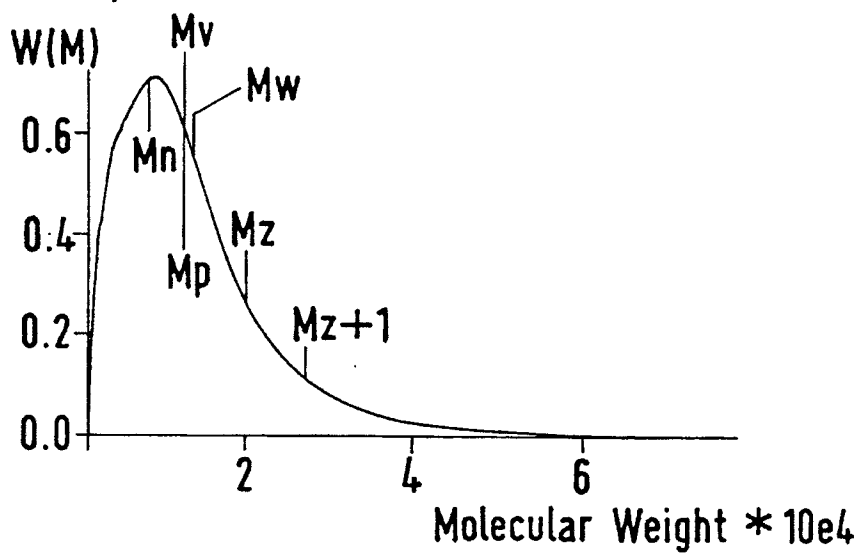
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FIG. 19 Example 6(d)*Raw Chromatogram:**W(M) plot:*

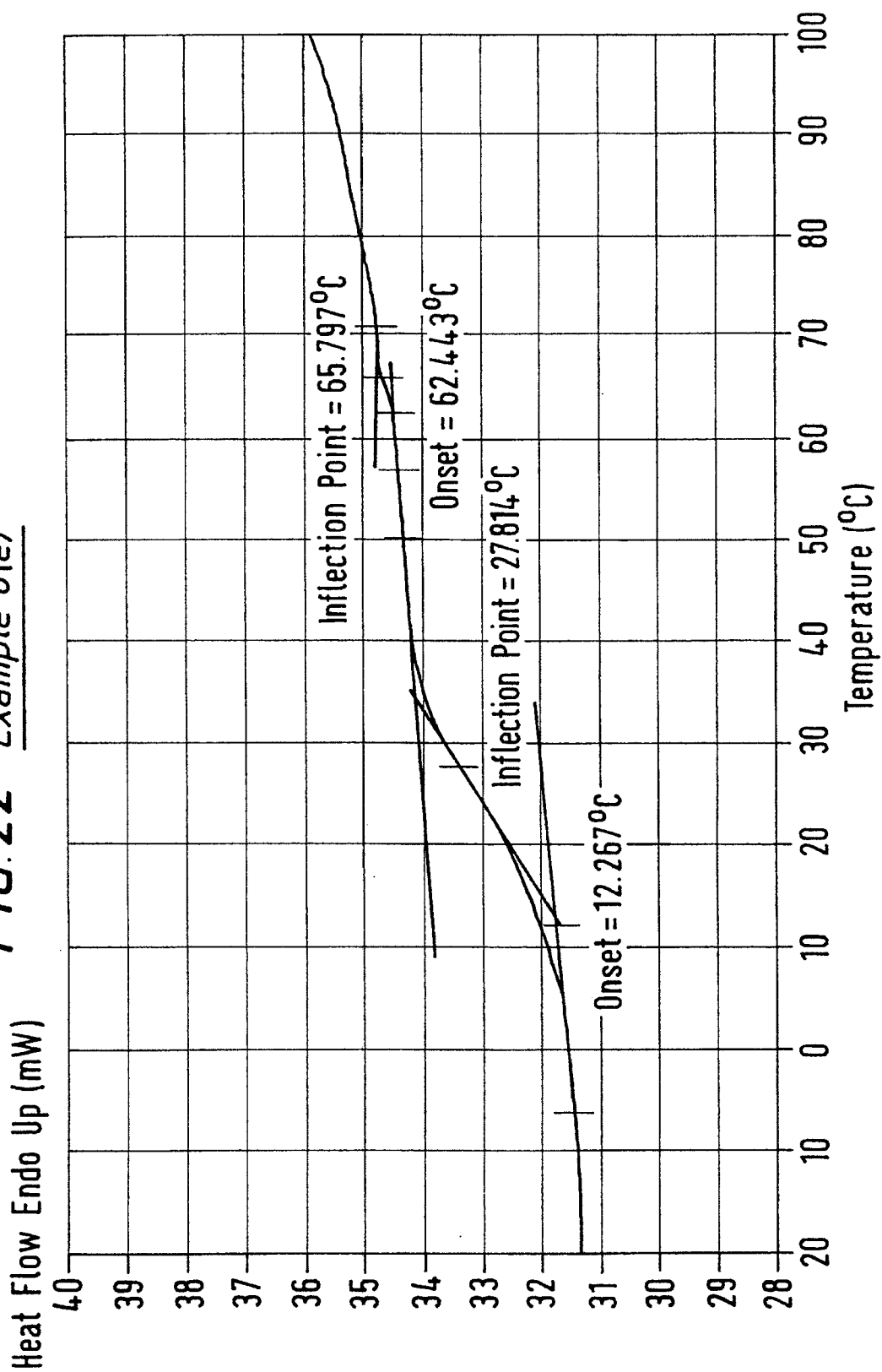
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FIG. 21 Example 6(e)*Raw Chromatogram:**W(M) plot:*

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FIG. 22 Example 6(e)

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FIG. 23 Example 6(e)